

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

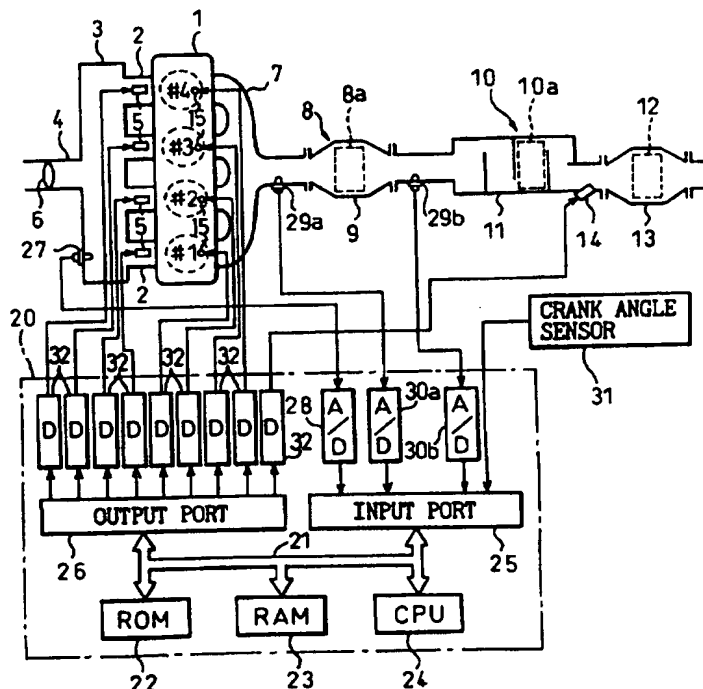

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : F01N 3/08, 9/00, B01D 53/94, F01N 3/28, 3/20		A1	(11) International Publication Number: WO 97/17532
(21) International Application Number: PCT/JP96/03205		(43) International Publication Date: 15 May 1997 (15.05.97)	
(22) International Filing Date: 31 October 1996 (31.10.96)		(74) Agents: ISHIDA, Takashi et al.; A. Aoki & Associates, Toranomon 37 Mori Building, 5-1, Toranomon 3-chome, Minato-ku, Tokyo 105 (JP).	
(30) Priority Data: 7/291258 9 November 1995 (09.11.95) JP 8/66806 22 March 1996 (22.03.96) JP 8/89572 11 April 1996 (11.04.96) JP		(81) Designated States: AU, CA, CN, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(71) Applicant (for all designated States except US): TOYOTA JIDOSHA KABUSHIKI KAISHA [JP/JP]; 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(72) Inventors; and (75) Inventors/Applicants (for US only): FUWA, Naohide [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP). TANAKA, Hiroshi [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP). KINUGASA, Yukio [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP). ITOU, Takaaki [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP). SUZUKI, Naoto [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP). YAEHASHI, Takehisa [JP/JP]; Toyota Jidosha Kabushiki Kaisha, 1, Toyota-cho, Toyota-shi, Aichi 471-71 (JP).			

(54) Title: METHOD AND DEVICE FOR PURIFYING EXHAUST GAS OF ENGINE

(57) Abstract

An exhaust manifold (7) of an engine (1) is connected to a three way (TW) catalyst (8a), and the TW catalyst (8a) is connected to an NH₃ adsorbing and oxidizing (NH₃-AO) catalyst (10a). The engine (1) performs the lean and the rich engine operations alternately and repeatedly. When the engine (1) performs the rich operation and thereby the exhaust gas air-fuel ratio of the exhaust gas flowing into the TW catalyst (8a) is made rich, NO_x in the inflowing exhaust gas is converted to NH₃ in the TW catalyst (8a). The NH₃ is then adsorbed in the NH₃-AO catalyst (10a). Next, when the engine (1) performs the lean operation and thereby the exhaust gas air-fuel ratio of the exhaust gas flowing into the TW catalyst (8a) is made lean, NO_x in the exhausted gas passes through the TW catalyst (8a), and flows into the NH₃-AO catalyst (10a). At this time, NH₃ adsorbed in the catalyst (10a) is desorbed therefrom, and reduces the inflowing NO_x.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

WO 97/17532

PCT/JP96/03205

- 1 -

DESCRIPTION

Method and Device for Purifying Exhaust Gas of Engine

5

TECHNICAL FIELD

The present invention relates to a method and a device for purifying an exhaust gas of an engine.

BACKGROUND ART

10 If an air-fuel ratio of an air-fuel mixture in a combustion chamber of an internal combustion engine is referred as an engine air-fuel ratio, an exhaust gas purifying device for an internal combustion engine with multi-cylinder has been known, in which a three-way catalyst is arranged in an exhaust passage, and the engine air-fuel ratio is controlled to be stoichiometric or rich with respect to the stoichiometric air-fuel ratio. If the engine air-fuel ratio is made lean with respect to the stoichiometric air-fuel ratio, the three way catalyst does not purify nitrogen oxides NO_x in the exhaust gas sufficiently, and thus the NO_x is emitted to the ambient air. Accordingly, the exhaust gas purifying device mentioned above makes the engine air-fuel ratio stoichiometric or rich, to thereby purify NO_x, at the three-way catalyst, as much as possible.

20 On the other hand, a lower fuel consumption rate is desirable, and thus it is desirable to make the engine air-fuel ratio as lean as possible. However, if the engine air-fuel ratio is made lean, the above-mentioned exhaust gas purifying device cannot purify NO_x sufficiently. To solve this problem, Japanese Unexamined Patent Publication No. 4-365920 discloses an exhaust gas purifying device for an internal combustion engine with multi-cylinders, the engine having first and second cylinder groups. The purifying device is provided with; an engine operation control device to continuously make

each cylinder operation of the first cylinder group a rich engine operation in which the engine air-fuel ratio is rich, and to continuously make each cylinder operation of the second cylinder group a lean engine operation in which the engine air-fuel ratio is lean; a first exhaust passage connected to each cylinder of the first cylinder group; a second exhaust passage connected to each cylinder of the second cylinder group and different from the first exhaust passage; an NH_3 synthesizing catalyst arranged in the first exhaust passage for synthesizing ammonium NH_3 from at least a part of NO_x in the inflowing exhaust gas; an interconnecting passage interconnecting the first exhaust passage downstream of the NH_3 synthesizing catalyst and the second exhaust passage to each other; and an exhaust gas purifying catalyst arranged in the interconnecting passage to react NO_x and NH_3 flowing therein to each other to thereby purify NO_x and NH_3 simultaneously. In this exhaust gas purifying device, the fuel consumption rate is reduced by increasing the numbers of the cylinders of the second cylinder group in which the lean engine operation is performed, while purifying NO_x by synthesizing NH_3 from NO_x exhausted from the first group and reacting the NH_3 and NO_x from the second group.

However, this device requires two, separate exhaust passages, one for the first cylinder group, and the other for the second cylinder group. This complicates the structure of the device, and makes the size of the device larger.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a method and a device for purifying an exhaust gas of an engine which can purify the exhaust gas sufficiently with a simple structure.

According to one aspect of the present invention, there is provided a method for purifying an exhaust gas

of an engine, comprising, in turn: forming an exhaust
gas portion of which an exhaust gas air-fuel ratio is
lean, and an exhaust gas portion of which the exhaust gas
air-fuel ratio is rich, from the exhaust gas of the
5 engine, alternately and repeatedly; and contacting the
exhaust gas portions an NH_3 synthesizing catalyst and an
exhaust gas purifying catalyst comprised of at least one
selected from the group consisted of an NH_3 adsorbing and
oxidizing (NH_3 -AO) catalyst and a NO_x occluding and
10 reducing (NO_x -OR) catalyst, in turn, the NH_3 synthesizing
catalyst synthesizing NH_3 from at least a part of NO_x in
the inflowing exhaust gas when the exhaust gas air-fuel
ratio of the inflowing exhaust gas is rich, and passing
 NO_x in the inflowing exhaust gas therethrough when the
15 exhaust gas air-fuel ratio of the inflowing exhaust gas
is lean, the NH_3 -AO catalyst adsorbing NH_3 in the
inflowing exhaust gas therein, and desorbing the adsorbed
 NH_3 therefrom and oxidizing the NH_3 when an NH_3
concentration in the inflowing exhaust gas becomes lower,
20 and the NO_x -OR catalyst occluding NO_x in the inflowing
exhaust gas therein when the exhaust gas air-fuel ratio
of the inflowing exhaust gas is lean, and releasing the
occluded NO_x therefrom and reducing the NO_x when the
exhaust gas air-fuel ratio of the inflowing exhaust gas
25 is rich.

According to another aspect of the present
invention, there is provided a device for purifying an
exhaust gas of an engine having an exhaust passage,
comprising: exhaust gas portion forming means arranged
30 in the engine or the exhaust passage for forming an
exhaust gas portion of which an exhaust gas air-fuel
ratio is lean, and an exhaust gas portion of which the
exhaust gas air-fuel ratio is rich, from the exhaust gas
of the engine, alternately and repeatedly; an NH_3
35 synthesizing catalyst arranged in the exhaust passage

downstream of the exhaust gas portion forming means, the
NH₃ synthesizing catalyst synthesizing NH₃ from at least
a part of NO_x in the inflowing exhaust gas when the
exhaust gas air-fuel ratio of the inflowing exhaust gas
5 is rich, and passing NO_x in the inflowing exhaust gas
therethrough when the exhaust gas air-fuel ratio of the
inflowing exhaust gas is lean; and an exhaust gas
purifying catalyst arranged in the exhaust passage
downstream of the NH₃ synthesizing catalyst, the exhaust
10 gas purifying catalyst comprising at least one selected
from the group consisting of an NH₃ adsorbing and
oxidizing (NH₃-AO) catalyst and a NO_x occluding and
reducing (NO_x-OR) catalyst, the NH₃-AO catalyst adsorbing
NH₃ in the inflowing exhaust gas therein, and desorbing
15 the adsorbed NH₃ therefrom and oxidizing the NH₃ when the
NH₃ concentration in the inflowing exhaust gas becomes
lower, and the NO_x-OR catalyst occluding NO_x in the
inflowing exhaust gas therein when the exhaust gas
air-fuel ratio of the inflowing exhaust gas is lean, and
20 releasing the occluded NO_x therefrom and reducing the NO_x
when the exhaust gas air-fuel ratio of the inflowing
exhaust gas is rich.

The present invention may be more fully understood
from the description of preferred embodiments of the
25 invention set forth below, together with the accompanying
drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a general view of an internal combustion
engine; Fig. 2A illustrates a characteristic of a
30 three-way catalyst; Fig. 2B illustrates a variation of a
NO_x amount exhaust from the engine with an engine
air-fuel ratio; Fig. 3 schematically illustrates a method
for purifying the exhaust gas according to the present
invention; Figs. 4A and 4B schematically illustrate the
35 exhaust gas purifying method in the engine shown in

Fig. 1; Fig. 5 is a time chart for explaining the exhaust gas purifying method in the engine shown in Fig. 1; Figs. 6A and 6B are diagrams illustrating the NO_x amount exhausted from the engine per unit time; Fig. 7 is a diagram illustrating the NH₃ synthesizing efficiency of the NH₃ synthesizing catalyst; Figs. 8A and 8B are diagrams illustrating the NH₃ amount desorbed from the NH₃ adsorbing and oxidizing catalyst per unit time; Figs. 9A and 9B are diagrams illustrating the temperatures of the exhaust gas; Fig. 10 is a flow chart for controlling the engine operation period; Fig. 11 is a flow chart for calculating the fuel injection time; Fig. 12 is a flow chart for controlling the ignition timing; Fig. 13 is a diagram illustrating a cylinder number ratio; Fig. 14 illustrates the lean and rich operation periods with $RATIO = 1$; Fig. 15 illustrates the lean and rich operation periods with $RATIO = 2$; Fig. 16 illustrates the lean and rich operation periods with $RATIO = 3$; Fig. 17 illustrates the lean and rich operation periods with $RATIO = 4$; Fig. 18 illustrates the relationship between $RATIO$ and $DRATIO$; Fig. 19 illustrates a method for calculating $DRICH$; Fig. 20 is a flow chart for controlling the engine operation period, using the ratio, according to another embodiment; Fig. 21 illustrates the lean and rich operation periods with $RATIO = 2$, according to further another embodiment; Fig. 22 illustrates the cylinder number ratio, according to another embodiment; Fig. 23 illustrates the lean air-fuel ratio, according to another embodiment; Fig. 24 illustrates the rich air-fuel ratio, according to another embodiment; Figs. 25A and 25B illustrate the rich air-fuel ratio, according to further another embodiment; Figs. 26 to 29 are time charts illustrating the variation in the target air-fuel ratio, according to further another embodiments, respectively; Fig. 30 is a diagram illustrating the changing rate of

the target air-fuel ratio; Fig. 31 is a flow chart for controlling the ignition timing in the embodiment shown in Fig. 26; Fig. 32 is a general view of an engine, according to a further another embodiment; Fig. 33 is a
5 general view of an engine, according to a further another embodiment; Figs. 34A and 34B is an illustration for explaining the NO_x occluding and reducing mechanism of the NO_x occluding and reducing catalyst; Figs. 35A and 35B schematically illustrate the exhaust gas
10 purifying method in the engine shown in Fig. 33; Figs. 36A and 36B are diagrams illustrating the NO_x amount released from the NO_x occluding and reducing catalyst per unit time; Fig. 37 is a diagram illustrating the temperature of the exhaust gas; Fig. 38A is a flow
15 chart for controlling the engine operation period in the engine shown in Fig. 33; Fig. 38B is a time chart for explaining the exhaust gas purifying method in the engine shown in Fig. 33; Fig. 39 is a general view of an engine, according to further another embodiment; Figs. 40A and
20 40B schematically illustrate the exhaust gas purifying method in the engine shown in Fig. 39; Figs. 41A and 41B illustrate other embodiments of the structure of the exhaust gas purifying catalyst, respectively; Fig. 42 is a general view of an engine according to a further
25 another embodiment; Fig. 43A is a time chart for explaining the exhaust gas purifying method in the engine shown in Fig. 42; Fig. 43B schematically illustrates the variation in the exhaust gas air-fuel ratio along the exhaust passage; Figs. 44 and 45 are flow charts for
30 calculating the fuel injection times of the engine and the auxiliary engine; Fig. 46 is a general view of the engine, according to a further another embodiment; Fig. 47 is a time chart for explaining the exhaust gas purifying method in the engine shown in Fig. 46; Fig. 48
35 is a general view of the engine, according to a further another embodiment; and Fig. 49 is a time chart for

explaining the exhaust gas purifying method in the engine shown in Fig. 48.

BEST MODE FOR CARRYING OUT THE INVENTION

In general, nitrogen oxides NO_x includes nitrogen
5 monoxide NO , nitrogen dioxide NO_2 , dinitrogen tetroxide N_2O_4 , dinitrogen monoxide N_2O , etc. The following explanation is made referring NO_x mainly as nitrogen monoxide NO and/or nitrogen dioxide NO_2 , but a method and
10 a device for purifying an exhaust gas of an engine according to the present invention can purify the other nitrogen oxides.

Fig. 1 shows the case where the present invention is applied to an internal engine of the spark ignition type. However, the present invention may be applied to a diesel
15 engine. Also, the engine shown in Fig. 1 is used for an automobile, for example.

Referring to Fig. 1, an engine body 1, which is a spark-ignition type engine, has four cylinders, i.e., a first cylinder #1, a second cylinder #2, a third
20 cylinder #3, a fourth cylinder #4. Each cylinder #1 to #4 is connected to a common surge tank 3, via a corresponding branch 2, and the surge tank 3 is connected to a air-cleaner (not shown) via an intake duct 4. In each branch 2, a fuel injector 5 is arranged to feed
25 fuel, such as gasoline, to the corresponding cylinder. Further, a throttle valve 6 is arranged in the intake duct 4, an opening of which becomes larger as the depression of the acceleration pedal (not shown) becomes larger. Note that the fuel injectors 5 are controlled in
30 accordance with the output signals from an electronic control unit 20.

On the other hand, each cylinder is connected to a common exhaust manifold 7, and the exhaust manifold 7 is connected to a catalytic converter 9 housing an NH_3
35 synthesizing catalyst 8 therein. The catalytic converter 9 is then connected to a muffler 10 housing an

exhaust gas purifying catalyst 10 therein. The muffler 10 is then connected to a catalytic converter 13 housing an NH_3 purifying catalyst 12 therein. Further, as shown in Fig. 1, a secondary air supplying device 14 is arranged in the exhaust passage between the muffler 11 and the catalytic converter 13, for supplying a secondary air to the NH_3 purifying catalyst 12, and is controlled in accordance with the output signals from the electronic control unit 20. Further, each cylinder #1 to #4 is provided with a spark plug 15, which is controlled in accordance with the output signals from the electronic control unit 20.

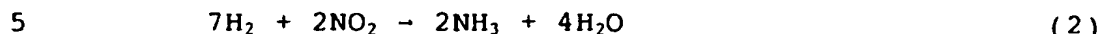
The electronic control unit 20 comprises a digital computer and is provided with a ROM (read only memory) 22, a RAM (random access memory) 23, a CPU (micro processor) 24, an input port 25, and an output port 26, which are interconnected by a bidirectional bus 21. Mounted in the surge tank 3 is a pressure sensor 27 generating an output voltage proportional to a pressure in the surge tank 3. The output voltage of the sensor 27 is input via an AD converter 28 to the input port 25. The intake air amount Q is calculated in the CPU 24 on the basis of the output signals from the AD converter 28. Further, mounted in the collecting portion of the exhaust manifold 7 is an upstream side air-fuel ratio sensor 29a generating an output voltage proportional to an exhaust gas air-fuel ratio, explained hereinafter, of the exhaust gas flowing through the collecting portion of the exhaust manifold 7. The output voltage of the sensor 29a is input via an AD converter 30a to the input port 25. Mounted in the exhaust passage between the catalytic converter 9 and the muffler 11 is a downstream side air-fuel ratio sensor 29b generating an output voltage proportional to the exhaust gas air-fuel ratio of the exhaust gas flowing in that exhaust passage, that is, exhausted from the NH_3 synthesizing catalyst 8. The

output voltage of the sensor 29b is input via an AD converter 30b to the input port 25. Further, connected to the input port 25 is a crank angle sensor 31 generating an output pulse whenever the crank shaft of the engine 1 turns by, for example, 30 degrees. The CPU 24 calculates the engine speed N in accordance with the pulse. On the other hand, the output port 26 is connected to the fuel injectors 5, the spark plugs 15, and the secondary supplying device 14, via corresponding drive circuits 32.

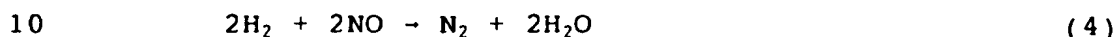
In the embodiment shown in Fig. 1, the NH_3 synthesizing catalyst 8 is comprised of a three-way catalyst 8a, which is simply expressed as a TW catalyst, here. The TW catalyst 8a is comprised of precious metals such as palladium Pd, platinum Pt, and rhodium Rh, carried on a layer of, for example, alumina, formed on a surface of a substrate.

Fig. 2A illustrates the purifying efficiency of the exhaust gas of the TW catalyst 8a. If a ratio of the total amount of air fed into the intake passage, the combustion chamber, and the exhaust passage upstream of a certain position in the exhaust passage to the total amount of fuel fed into the intake passage, the combustion chamber, and the exhaust passage upstream of the above-mentioned position is referred to as an exhaust gas air-fuel ratio of the exhaust gas flowing through the certain position, Fig. 2A shows that the TW catalyst 8a passes the inflowing NO_x therethrough when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean with respect to the stoichiometric air-fuel ratio $(\text{A/F})_S$, which is about 14.6 and the air-excess ratio $\lambda = 1.0$, and the TW catalyst 8a synthesizes NH_3 from a part of the inflowing NO_x when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich. The NH_3 synthesizing function of the TW catalyst 8a is unclear, but it can be considered that some of NO_x in the exhaust gas of which

the exhaust gas air-fuel ratio is rich is converted to NH_3 according to the following reactions (1) and (2), that is:



On the contrary, it is considered that the other NO_x is reduced to the nitrogen N_2 according to the following reactions (3) to (6), that is:



Accordingly, NO_x flowing in the TW catalyst 8a is converted to either NH_3 or N_2 when the exhaust gas
15 air-fuel ratio of the inflowing exhaust gas is rich, and thus NO_x is prevented from being discharged from the TW catalyst 8a.

As shown in Fig. 2A, an efficiency ETA of the NH_3 synthesizing of the TW catalyst 8a becomes larger as the
20 exhaust gas air-fuel ratio of the inflowing exhaust gas becomes smaller or richer from the stoichiometric air-fuel ratio (A/F)_S, and is kept constant when the exhaust gas air-fuel ratio of the inflowing exhaust gas becomes even smaller. In the example shown in Fig. 2A,
25 the NH_3 synthesizing efficiency ETA is kept constant when the exhaust gas air-fuel ratio of the inflowing exhaust gas equals or is smaller than about 13.8, where the air-excess ratio λ is about 0.95).

On the other hand, the NO_x amount exhausted from
30 each cylinder per unit time depends on the engine air-fuel ratio, as shown in Fig. 2B. In particular, the exhausted NO_x amount becomes smaller as the engine air-fuel ratio becomes smaller when the engine air-fuel ratio is rich. Therefore, considering the synthesizing
35 efficiency ETA, the NH_3 amount synthesized in the TW

catalyst 8a per unit time reaches the maximum amount thereof when the exhaust gas air-fuel ratio of the inflowing exhaust gas is about 13.8, if the exhaust gas air-fuel ratio of the inflowing exhaust gas conforms to the engine air-fuel ratio.

Note that, in the engine shown in Fig. 1, it is desired to synthesize NH_3 in as large amount as possible, when the exhaust gas air-fuel ratio of the exhaust gas flowing the TW catalyst 8a is rich, because of the reasons described below. Accordingly, a TW catalyst carrying palladium Pd or cerium Ce is used as the TW catalyst 8a. In particular, a TW catalyst carrying palladium Pd can also enhance a HC purifying efficiency, when the exhaust air-fuel ratio of the inflowing exhaust gas is rich. Further, note that a TW catalyst carrying rhodium Rh suppresses an NH_3 synthesizing therein, and a TW catalyst without rhodium Rh is desired used as the TW catalyst 8a.

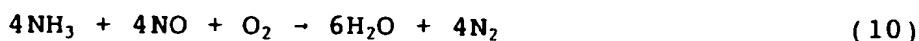
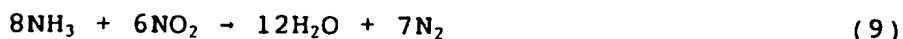
On the other hand, in the embodiment shown in Fig. 1, the exhaust gas purifying catalyst 10 is consisted of an NH_3 adsorbing and oxidizing catalyst 10a, which is simply expressed as a NH_3 -AO catalyst. The NH_3 -AO catalyst 10a is comprised of a so-called zeolite denitration catalyst, such as zeolite carrying copper Cu thereon, zeolite carrying copper Cu and platinum Pt thereon, and zeolite carrying iron Fe thereon, which is carried on a surface of a substrate. Alternatively, the NH_3 -AO catalyst 10a is comprised of solid acid such as zeolite, silica, silica-alumina, and titania, carrying the transition metals such as iron Fe and copper Cu or precious metals such as palladium Pd, platinum Pt and rhodium Rh.

The NH_3 -AO catalyst 10a adsorbs NH_3 in the inflowing exhaust gas, and desorbs the adsorbed NH_3 when the NH_3 concentration in the inflowing exhaust gas becomes lower, or when the inflowing exhaust gas includes NO_x . At this

time, if the NH_3 -AO catalyst 10a is under the oxidizing atmosphere, that is, if the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, the NH_3 -AO catalyst 10a oxidizes all of NH_3 desorbed therefrom.

5 Also, if the inflowing exhaust gas includes both of NH_3 and NO_x , the NH_3 -AO catalyst 10a oxidizes NH_3 by NO_x . In these cases, the NH_3 oxidizing function has a portion which has been unclear, but it can be considered that the NH_3 oxidation occurs according to the following

10 reactions (7) to (10), that is:



15 The reactions (9) and (10), which are denitration, reduce both of NO_x produced in the oxidation reactions (7) and (8), and NO_x in the exhaust gas flowing in the NH_3 -AO catalyst 10a.

20 It has been found, by experiment, that the NH_3 -AO catalyst 10a of this embodiment performs good oxidation and denitration when the temperature of the inflowing exhaust gas is about 300 to 500°C. On the other hand, in general, the temperature of the exhaust gas passing through the muffler 11 is about 300 to 500°C. Therefore, 25 in this embodiment, the NH_3 -AO catalyst 10a is arranged in the muffler 11 to thereby ensure the good performance of the NH_3 -AO catalyst 10a.

30 The NH_3 purifying catalyst 12 is comprised of transition metals such as iron Fe and copper Cu, or precious metals such as palladium Pd, platinum Pt, and rhodium Rh, carried on a layer of, for example, alumina, formed on a surface of a substrate. The NH_3 purifying catalyst 12 purifies or resolves NH_3 in the inflowing exhaust gas, if the catalyst 12 is under the oxidizing 35 atmosphere, that is, if the exhaust gas air-fuel ratio of

the inflowing exhaust gas is lean. In this case, it is considered that the oxidation and denitration reactions (7) to (10) mentioned above occur in the catalyst 12 and thereby NH_3 is purified or resolved. In this embodiment, basically, the NH_3 amount exhausted from the NH_3 -AO catalyst 10a is kept zero, but the NH_3 purifying catalyst 12 prevents NH_3 from being emitted to the ambient air, even if NH_3 is discharged from the NH_3 -AO catalyst 10a without being purified.

In the engine shown in Fig. 1, the fuel injection time TAU is calculated using the following equation:

$$\text{TAU} = \text{TB} \cdot ((\text{A/F})\text{S} / (\text{A/F})\text{T}) \cdot \text{FAF}$$

TB represents a basic fuel injection time suitable for making the engine air-fuel ratio of each cylinder equal to the stoichiometric air-fuel ratio $(\text{A/F})\text{S}$, and is calculated using the following equation:

$$\text{TB} = (\text{Q} / \text{N}) \cdot \text{K}$$

where Q represents the intake air amount, N represents the engine speed, and K represents a constant.

Accordingly, the basic fuel injection time TB is a product of an intake air amount per unit engine speed, and the constant.

$(\text{A/F})\text{T}$ represents a target value for the control of the engine air-fuel ratio. When the target value $(\text{A/F})\text{T}$ is made larger to make the engine air-fuel ratio lean with respect to the stoichiometric air-fuel ratio, the fuel injection time TAU is made shorter and thereby the fuel amount to be injected is decreased. When the target value $(\text{A/F})\text{T}$ is made smaller to make the engine air-fuel ratio rich with respect to the stoichiometric air-fuel ratio, the fuel injection time TAU is made longer and thereby the fuel amount to be injected is increased.

FAF represents a feedback correction coefficient for making the actual engine air-fuel ratio equal to the target value $(\text{A/F})\text{T}$. The feedback correction coefficient FAF is determined on the basis of the output signals from

the upstream side air-fuel ratio sensor 29a, mainly. The exhaust gas air-fuel ratio of the exhaust gas flowing through the exhaust manifold 7 and detected by the upstream side air-fuel ratio sensor 29a conforms to the engine air-fuel ratio. When the exhaust gas air-fuel ratio detected by the upstream side sensor 29a is lean with respect to the target value $(A/F)_T$, the feedback correction coefficient FAF is made larger and thereby the fuel amount to be injected is increased. When the exhaust gas air-fuel ratio detected by the sensor 29a is rich with respect to the target value $(A/F)_T$, FAF is made smaller and thereby the fuel amount to be injected is decreased. In this way, the actual engine air-fuel ratio is made equal to the target value $(A/F)_T$. Note that the feedback correction coefficient FAF fluctuates around 1.0.

Contrarily, the downstream side air-fuel ratio sensor 29b is for compensating for the deviation of the engine air-fuel ratio from the target value $(A/F)_T$ due to the deterioration of the upstream side sensor 29a. For the upstream side and the downstream side sensors 29a and 29b, an air-fuel ratio sensor generating an output voltage which corresponds to the exhaust gas air-fuel ratio over a broader range of the exhaust gas air-fuel ratio may be used, while a Z-output type oxygen concentration sensor, of which an output voltage varies drastically when the detecting exhaust gas air-fuel ratio increases or decreases across the stoichiometric air-fuel ratio, may also be used. Note that the downstream side sensor 29b may be arranged in the exhaust passage between the exhaust gas purifying catalyst 10 and the secondary air supplying device 14, alternatively. Further, the deterioration of the catalyst(s) located between the two sensors 29a and 29b may be detected on the basis of the output signals from the sensors 29a and 29b.

In the engine shown in Fig. 1, there is no device for supplying secondary fuel or secondary air in the

exhaust passage, other than the secondary air supplying device 14. Thus, the engine air-fuel ratio in the exhaust passage upstream of the secondary air supplying device 14 conforms to the engine air-fuel ratio. In other words, the exhaust gas air-fuel ratio of the exhaust gas flowing in the TW catalyst 8a conforms to the engine air-fuel ratio, and the exhaust gas air-fuel ratio of the exhaust gas flowing in the exhaust gas purifying catalyst 10 also conforms to the engine air-fuel ratio. Contrarily, in the exhaust passage downstream of the secondary air supplying device 14, the exhaust gas air-fuel ratio conforms to the engine air-fuel ratio when the supply of the secondary air is stopped, and is made lean with respect to the engine air-fuel ratio when the secondary air is supplied.

Next, the exhaust gas purifying method in the engine shown in Fig. 1 will be explained with reference to Figs. 3, 4A, and 4B.

In the engine shown in Fig. 1, an exhaust gas portion of which the exhaust gas air-fuel ratio is lean, and an exhaust gas portion of which the exhaust gas air-fuel ratio is rich, are formed from the exhaust gas of the engine 1, alternately and repeatedly. Then, the exhaust gas portions are introduced to, in turn, the TW catalyst 8a, the exhaust gas purifying catalyst 10, and the NH_3 purifying catalyst 12. In other words, the exhaust gas air-fuel ratio of the exhaust gas flowing the catalysts 8a and 10a is made lean and rich alternately and repeatedly, as shown in Fig. 3. When the exhaust gas air-fuel ratio of the inflowing exhaust gas is made rich, the TW catalyst 8a converts NO_x in the inflowing exhaust gas to NH_3 or N_2 , as shown in Fig. 4A, according to the above-mentioned reactions (1) and (2). The NH_3 synthesized in the TW catalyst 8a then flows into the NH_3 -AO catalyst 10a. At this time, the concentration of NH_3 in the inflowing exhaust gas is relatively high, and

thus almost all of NH_3 in the inflowing exhaust gas is adsorbed in the NH_3 -AO catalyst 10a. Even though NH_3 flows out the NH_3 -AO catalyst 10a without being adsorbed, the NH_3 then flows into the NH_3 purifying catalyst 12 and is purified or oxidized, because the catalyst 12 is kept under the oxidizing atmosphere by the secondary air supplying device 14. In this way, NH_3 is prevented from being emitted to the ambient air.

Contrarily, when the exhaust gas air-fuel ratio of the inflowing exhaust gas is made lean, the TW catalyst 8a passes the inflowing NO_x therethrough, as shown in Fig. 4B, and the NO_x then flows into the NH_3 -AO catalyst 10a. At this time, the NH_3 concentration in the inflowing exhaust gas is substantially zero, and thus NH_3 is desorbed from the NH_3 -AO catalyst 10a. At this time, the NH_3 -AO catalyst 10a is under the oxidizing atmosphere, and thus the desorbed NH_3 acts as a reducing agent, and reduces and purifies NO_x in the inflowing exhaust gas, according to the above-mentioned reactions (7) to (10). Note that, even if the NH_3 amount desorbed from the NH_3 -AO catalyst 10a exceeds over the amount required for reducing the inflowing NO_x , the excess NH_3 is purified or resolved in the NH_3 -AO catalyst 10a or the NH_3 purifying catalyst 12. Accordingly, NH_3 is prevented from being emitted to the ambient air. Note that, in this case, the secondary air is unnecessary.

As mentioned above, NO_x exhausted from the engine is reduced to N_2 or adsorbed in the NH_3 -AO catalyst 10a in the form of NH_3 when the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is rich, and is reduced to N_2 by NH_3 desorbed from the NH_3 -AO catalyst 10a when the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is

lean. Accordingly, NO_x is prevented from being emitted to the ambient air, regardless whether the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is rich or lean.

5 Note that, as mentioned above, it is desired that the NH₃ purifying catalyst 12 is kept under the oxidizing atmosphere to ensure good NH₃ purification. In this embodiment, the secondary air supplying device 14
10 supplies the secondary air to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH₃ purifying catalyst 12 equal to about 15.3 ($\lambda = 1.05$).

 As long as the exhaust gas air-fuel ratio of the exhaust gas flowing into the TW catalyst 8a is kept lean, unburned hydrocarbon HC and/or carbon monoxide, etc. in
15 the inflowing exhaust gas are oxidized and purified at the TW catalyst 8a. Contrarily, when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, there may be the case where the HC and/or the CO passes through the TW catalyst 8a and the NH₃-AO catalyst 10a.
20 However, the HC and/or the CO then flows into the NH₃ purifying catalyst 12 and are oxidized and purified sufficiently, because the catalyst 12 is kept under the oxidizing atmosphere, as mentioned above.

 To form the exhaust gas portions of which the
25 exhaust gas air-fuel ratios are lean and rich respectively, there may be provided a secondary air supplying device for supplying the secondary air in, for example, the exhaust manifold 7. In this case, while the engine air-fuel ratio is kept rich, the supply of the
30 secondary air is stopped to thereby form the exhaust gas portion of which exhaust gas air-fuel ratio is rich, and the secondary air is supplied to thereby form the exhaust gas portion of which exhaust gas air-fuel ratio is lean. Or, there may be provided a secondary fuel supplying
35 device for supplying the secondary fuel in, for example, the exhaust manifold 7. In this case, while the engine

air-fuel ratio is kept lean, the supply of the secondary fuel is stopped to thereby form the exhaust gas portion of which exhaust gas air-fuel ratio is lean, and the secondary fuel is supplied to thereby form the exhaust gas portion of which exhaust gas air-fuel ratio is rich.

However, as mentioned above, the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a conforms to the engine air-fuel ratio, in the engine shown in Fig. 1. Therefore, the engine air-fuel ratio is controlled to be lean and rich alternately and repeatedly to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean and rich alternately and repeatedly. Namely, the engine 1 operates in a lean engine operation in which the engine air-fuel ratio is lean to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean, and the engine 1 operates in a rich engine operation in which the engine air-fuel ratio is rich to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a rich, and the engine 1 operates in the lean and rich engine operations alternately and repeatedly.

In other words, NO_x exhausted from the engine 1 is purified sufficiently and is prevented from being emitted to the ambient air, by the engine operating the lean and rich engine operations alternately and repeatedly.

If a target value of the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is referred to as a target air-fuel ratio $(A/F)_T$, the actual exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is made equal to the target air-fuel ratio $(A/F)_T$, by making the target value of the engine air-fuel ratio equal to the target air-fuel ratio $(A/F)_T$. Therefore, in the embodiment, the target value of the engine air-fuel ratio is conformed to

the target air-fuel ratio (A/F)T. The target air-fuel ratio (A/F)T is made equal to a lean air-fuel ratio (A/F)L which is lean with respect to the stoichiometric air-fuel ratio (A/F)S, and equal to a rich air-fuel ratio (A/F)R which is rich with respect to the stoichiometric air-fuel ratio (A/F)S, alternately and repeatedly, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean and rich alternately and repeatedly. Note that, if an engine operation period during which the engine performs the lean engine operation is referred as a lean operation period TL, and if an engine operation period during which the engine performs the rich engine operation is referred as a rich operation period TR, one lean operation period TL and one rich operation period TR, next to each other, form a cycle.

The lean air-fuel ratio (A/F)L and the rich air-fuel ratio (A/F)R may be determined in accordance with the engine operating condition, respectively. However, in the present embodiment, the lean air-fuel ratio (A/F)L is set constant at about 25.0, and the rich air-fuel ratio (A/F)R is set constant at about 13.8, regardless the engine operating condition. Therefore, the target air-fuel ratio (A/F)T is made equal to about 25.0 when the lean engine operation is to be performed, and is made equal to about 13.8 when the rich engine operation is to be performed.

If the air-fuel mixture spreading over the entire combustion chamber uniformly is formed when the engine air-fuel ratio is very lean, such as 25.0, the spark plug 15 cannot ignite the air-fuel mixture, because the air-fuel mixture is very thin, and misfiring may occur. To solve this, in the engine shown in Fig. 1, an ignitable air-fuel mixture is formed in a restricted region in the combustion chamber and the reminder is filled with only the air or only the air and the EGR gas, and the air-fuel mixture is ignited by the spark plug 15,

when the lean engine operation is to be performed. This prevents the engine from misfiring, even though the engine air-fuel ratio is very lean. Alternatively, the misfiring may be prevented by forming the swirl flow in the combustion chamber, while forming the uniform air-fuel mixture in the combustion chamber.

As mentioned at the beginning, a lower fuel consumption rate is desired, and thus it is desired to make the lean operation period TL as long as possible, and to make the rich operation period TR as short as possible. In particular, it is preferable that TL/TR is equal to or larger than 3, for the lesser fuel consumption rate. However, as the lean operation period TL becomes longer, the NH_3 amount desorbed from the NH_3 -AO catalyst 10a becomes smaller. Thus, a longer lean operation period TL may lead to a lack of NH_3 for purifying NO_x in the NH_3 -AO catalyst 10a, and to the emit NO_x to the ambient air without reduction. To solve this, in this embodiment, an NH_3 amount adsorbed in the NH_3 -AO catalyst 10a $S(\text{NH}_3)$ is obtained by obtaining an NH_3 amount desorbed from the NH_3 -AO catalyst 10a during the lean engine operation, and the lean engine operation is stopped and the rich engine operation starts when the adsorbed NH_3 amount $S(\text{NH}_3)$ becomes smaller than a predetermined minimum amount $\text{MIN}(\text{NH}_3)$. This prevents NO_x flowing into the NH_3 -AO catalyst 10a from being emitted to the ambient air without being reduced.

On the other hand, the shorter rich operation period is preferable. However, if the rich operation period TR is made too short, the adsorbed NH_3 amount $S(\text{NH}_3)$ may be smaller than that required for the sufficient reduction of NO_x , and thereby NO_x may be discharged without being reduced when the NO_x amount inflowing the NH_3 -AO catalyst 10a increases drastically. Further, too short a rich operation period may lead to frequent changes in the

target air-fuel ratio (A/F)_T between the lean and rich air-fuel ratios, and thus an undesired deterioration of the drivability may occur. However, if the rich operation period TR becomes longer, the NH₃-AO catalyst 10a is saturated with NH₃, and a large amount of NH₃ is discharged therefrom. To solve this, in this embodiment, the NH₃ amount adsorbed in the NH₃-AO catalyst 10a during the rich engine operation is obtained to thereby obtain the adsorbed NH₃ amount S(NH₃), and the rich engine operation is stopped and the lean engine operation is started when the adsorbed NH₃ amount S(NH₃) becomes larger than a maximum amount MAX(NO_x), which is determined in accordance with the adsorbing capacity of the NH₃-AO catalyst 10a. In this way, the lean and the rich operation periods TL and TR are determined in accordance with the adsorbed NH₃ amount S(NH₃) of the NH₃-AO catalyst 10a, in the present embodiment.

It is difficult to directly find the adsorbed NH₃ amount in the NH₃-AO catalyst 10a. Therefore, in this embodiment, the adsorbed NH₃ amount is estimated on the basis of the NH₃ amount synthesized in the TW catalyst 8a or flowing into the NH₃-AO catalyst 10a. In this case, a sensor for detecting the NH₃ amount flowing into the NH₃-AO catalyst 10a may be arranged in the exhaust passage between the TW catalyst 8a and the NH₃-AO catalyst 10a. However, in the embodiment, considering the applicability, the synthesized NH₃ amount is estimated on the basis of the NO_x amount flowing into the TW catalyst 8a, and then the adsorbed NH₃ amount is estimated on the basis of the synthesized NH₃ amount. That is, the synthesized NH₃ amount per unit time becomes larger as the NO_x amount flowing into the TW catalyst 8a per unit time becomes larger. Also, the synthesized NH₃ amount per unit time becomes larger as the synthesizing

efficiency ETA becomes higher.

On the other hand, the NO_x amount exhausted from the engine per unit time becomes larger as the engine speed N becomes higher, and thus the NO_x amount flowing into the TW catalyst 8a per unit time becomes larger. Also, the exhaust gas amount exhausted from the engine becomes larger and the combustion temperature becomes higher as the engine load Q/N (the intake air amount Q / the engine speed N) becomes higher, and thus the NO_x amount flowing into the TW catalyst 8a per unit becomes larger as the engine load Q/N becomes higher.

Fig. 6A illustrates the relationships, obtained by experiments, between the NO_x amount exhausted from the engine per unit time $Q(\text{NO}_x)$, the engine load Q/N , and the engine speed N , with a constant lean or rich air-fuel ratio $(A/F)_L$ or $(A/F)_R$. In Fig. 6A, the curves show the identical NO_x amount. As shown in Fig. 6A, the exhausted NO_x amount $Q(\text{NO}_x)$ becomes larger as the engine load Q/N becomes higher, and as the engine speed N becomes higher. Note that the exhausted NO_x amount $Q(\text{NO}_x)$ is stored in the ROM 22 in advance in the form of a map as shown in Fig. 6B.

The synthesizing efficiency ETA varies in accordance with the temperature TTC of the exhaust gas flowing into the TW catalyst 8a, which represents the temperature of the TW catalyst 8a. That is, as shown in Fig. 7, the synthesizing efficiency ETA becomes higher as the exhaust gas temperature TTC becomes higher when TTC is low, and becomes lower as TTC becomes higher when TTC is high, with the constant rich air-fuel ratio $(A/F)_R$. The synthesizing efficiency ETA is stored in the ROM 22 in advance in the form of a map as shown in Fig. 7.

Note that the exhausted NO_x amount from the engine per unit time $Q(\text{NO}_x)$ varies in accordance with the engine air-fuel ratio, as described above with reference to Fig. 2B. Therefore, if the lean or rich air-fuel ratio

(A/F)L, (A/F)R is changed in accordance with, for example, the engine operating condition, the exhausted NO_x amount Q(NO_x) obtained by the map shown in Fig. 6B must be corrected on the basis of the actual lean or rich air-fuel ratio (A/F)L, (A/F)R. Further, the synthesizing efficiency ETA also varies in accordance with the exhaust gas air-fuel ratio of the exhaust gas flowing into the TW catalyst 8a, that is, the rich air-fuel ratio (A/F)R, as shown in Fig. 2A. Therefore, if the rich air-fuel ratio (A/F)R is changed in accordance with, for example, the engine operating condition, the synthesizing efficiency ETA obtained by the map shown in Fig. 7 is also required to be corrected on the basis of the actual rich air-fuel ratio (A/F)R.

The product of Q(NO_x) calculated using the engine load Q/N and the engine speed N and the synthesizing efficiency ETA calculated using the exhaust gas temperature TTC represents the NH₃ amount flowing into the NH₃-AO catalyst 10a per unit time. Accordingly, during the rich engine operation, the NH₃ amount adsorbed in the NH₃-AO catalyst 10a is calculated using the following equation:

$$S(\text{NH}_3) = S(\text{NH}_3) + Q(\text{NO}_x) \cdot \text{ETA} \cdot \text{DELTAa}$$

where DELTAa represents the time interval of calculation of Q(NO_x) and ETA. Thus, Q(NO_x) · ETA · DELTAa represents the NH₃ amount adsorbed in the NH₃-AO catalyst 10a from the last calculation of Q(NO_x) and ETA until the present calculation.

Fig. 8A illustrates the NH₃ amount D(NH₃) desorbed from the NH₃-AO catalyst 10a per unit time, when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH₃-AO catalyst 10a is changed from rich to lean, obtained by experiment. In Fig. 8A, the curves show the identical desorbed NH₃ amount. As shown in Fig. 8A, the desorbed NH₃ amount D(NH₃) becomes larger as

the adsorbed NH_3 amount $S(\text{NH}_3)$ becomes larger. Also, $D(\text{NH}_3)$ becomes larger as the temperature TAC of the exhaust gas flowing into the NH_3 -AO catalyst 10a, which represents the temperature of the NH_3 -AO catalyst 10a, becomes higher. The desorbed NH_3 amount $D(\text{NH}_3)$ is stored in the ROM 22 in advance in the form of a map as shown in Fig. 8B.

Accordingly, during the lean engine operation, the adsorbed NH_3 amount $S(\text{NH}_3)$ is calculated using the following equation:

$$S(\text{NH}_3) = S(\text{NH}_3) - D(\text{NH}_3) \cdot \text{DELTA}d$$

where DELTA d represents the time interval of the calculation of $D(\text{NH}_3)$, and thus $D(\text{NH}_3) \cdot \text{DELTA}d$ represents the NH_3 amount desorbed from the NH_3 -AO catalyst 10a, from the last calculation of $D(\text{NH}_3)$ until the present calculation.

To obtain the temperature TTC of the exhaust gas flowing into the TW catalyst 8a, and the temperature TAC of the exhaust gas flowing into the NH_3 -AO catalyst 10a, temperature sensors may be arranged in the exhaust passage directly upstream of the TW catalyst 8a and directly upstream of the NH_3 -AO catalyst 10a, respectively. However, the exhaust gas temperatures can be estimated on the basis of the engine operating condition, that is, the engine load Q/N and the engine speed N . Thus, in the engine shown in Fig. 1, TTC and TAC are stored in the ROM 22 in advance in the form of a map as shown in Figs. 9A and 9B. ETA and $D(\text{NH}_3)$ are calculated using TTC and TAC obtained from the maps shown in Figs. 9A and 9B.

In this embodiment, one lean operation period TL is performed for several minutes, and one rich operation period is performed for several seconds, for example. Therefore, in this embodiment, the engine 1 performs the lean engine operation basically, and performs the rich

engine operation temporarily. In this case, a plurality of cylinders perform the lean engine operation during the lean engine operation, and a plurality of cylinders perform the rich engine operation during the rich engine operation. Note that the lean and the rich operation periods may be predetermined as a time. Further, alternatively, first, the total NO_x amount flowing into the NH_3 -AO catalyst 10a during the lean engine operation may be found, and the lean operation period TL may be set so that the total inflowing NO_x amount does not exceed a NO_x amount which NH_3 adsorbed in the NH_3 -AO catalyst 10a can purify.

Next, the control of the ignition timing in the engine shown in Fig. 1 will be explained with reference to Fig. 5.

In the engine shown in Fig. 1, the ignition timing IT in the lean engine operation is made ITL which provides, for example, the suitable output torque of the engine. On the contrary, the ignition timing IT in the rich engine operation is made ITR which is retarded with respect to the ignition timing ITL. Retarding the ignition timing suppresses the increase of the output torque, and thereby suppresses the undesired fluctuation in the output torque when the engine performs the lean and rich engine operations alternately and repeatedly. Further, retarding the ignition timing increases the temperature of the exhaust gas flowing into the TW catalyst 8a, and thereby the synthesized NH_3 amount is kept larger. As a result, the NH_3 amount for purifying NO_x increases without extending the rich operation period TR. Note that the ignition timing in the lean engine operation ITL is set in accordance with the engine operating condition, such as the lean air-fuel ratio (A/F)L. Also, the ignition timing in the rich engine operation ITR is set in accordance with the engine operating condition, such as the rich air-fuel ratio

(A/F)R and the ignition timing ITL.

Figs. 10 to 12 illustrate routines for executing the above-mentioned embodiment. Each routine is executed by interruption every predetermined crank angle.

5 Fig. 10 illustrates a routines for executing the control of the engine operation periods.

Referring to Fig. 10, first, in step 40, it is judged whether FRICH is made 1. FRICH is made 1 when the rich operation is to be performed, and is made zero when
10 the lean operation is to be performed. If FRICH is 1, that is, if the rich operation is to be performed, the routine goes to step 41, where the exhausted NO_x amount Q(NO_x) is calculated using the map shown in Fig. 6B on the basis of the engine load Q/N and the engine speed N.
15 In the following step 42, the exhaust gas temperature TTC is calculated using the map shown in Fig. 9A. In the following step 43, the NH₃ synthesizing efficiency ETA is calculated using the map shown in Fig. 7 on the basis of the exhaust gas temperature TTC. In the following
20 step 44, the adsorbed NH₃ amount S(NH₃) is calculated using the following equation:

$$S(NH_3) = S(NH_3) + Q(NO_x) \cdot ETA \cdot DELTAa$$

where DELTAa is a time interval from the last processing cycle until the present processing cycle, and is obtained
25 by, for example, a timer. In the following step 45, it is judged whether the adsorbed NH₃ amount S(NH₃) is larger than the maximum amount MAX(NH₃). If S(NH₃) ≤ MAX(NH₃), the processing cycle is ended. Namely, if S(NH₃) ≤ MAX(NH₃), the adsorbed NH₃ amount is judged to be
30 too small to purify NO_x, and thus the rich operation is continuously performed.

If S(NH₃) > MAX(NH₃), the routine goes to step 46, where FRICH is made zero, and then the processing cycle is ended. Namely, if S(NH₃) > MAX(NH₃), the adsorbed NH₃
35 amount is sufficient to purify NO_x, and the rich

operation is stopped and the lean operation starts (as at the time a, c, e, or g shown in Fig. 5). Accordingly, the rich operation period TR is a period from when FRICH is made 1 until $S(\text{NH}_3) > \text{MAX}(\text{NH}_3)$.

5 Contrarily, if $\text{FRICH} = 0$ in step 40, that is, if the lean operation is to be performed, the routine goes to step 47, where the exhaust gas temperature TAC is calculated using the map shown in Fig. 7B. In the following step 48, the desorbed NH_3 amount $D(\text{NH}_3)$ is
 10 calculated using the map shown in Fig. 8B, on the basis of TAC and the present $S(\text{NH}_3)$. In the following step 49, the adsorbed NH_3 amount $S(\text{NH}_3)$ is calculated using the following equation:

$$S(\text{NH}_3) = S(\text{NH}_3) - D(\text{NH}_3) \cdot \text{DELTA}d$$

15 where DELTAd is a time interval from the last processing cycle until the present processing cycle. In the following step 50, it is judged whether the adsorbed NH_3 amount $S(\text{NH}_3)$ is smaller than the minimum amount $\text{MIN}(\text{NH}_3)$. If $S(\text{NH}_3) \geq \text{MIN}(\text{NH}_3)$, the processing cycle is
 20 ended. Namely, if $S(\text{NH}_3) \geq \text{MIN}(\text{NH}_3)$, the adsorbed NH_3 amount $S(\text{NH}_3)$ is judged to be still large to purify NO_x , and thus the lean operation is continued.

If $S(\text{NH}_3) < \text{MIN}(\text{NH}_3)$, the routine goes to step 51, FRICH is made 1 and the processing cycle is ended.
 25 Namely, if $S(\text{NH}_3) < \text{MIN}(\text{NH}_3)$, the adsorbed NH_3 amount is judged to be insufficient to purify NO_x , and thus the lean operation is stopped and the rich engine operation starts (as at the time b, d, or f shown in Fig. 5). Accordingly, the lean operation period TL is from when
 30 the FRICH is made zero until $S(\text{NH}_3) < \text{MIN}(\text{NH}_3)$.

Fig. 11 illustrates the routine for calculating the fuel injection time TAU.

Referring to Fig. 11, first, in step 60, the basic fuel injection time TB is calculated using the following
 35 equation, on the basis of the engine load Q/N and the

engine speed N:

$$TB = (Q / N) \cdot K$$

In the following step 61, the feedback correction coefficient FAF is calculated. In the following step 62, it is judged whether FRICH, which is controlled in the routine shown in Fig. 10, is made 1. If FRICH = 1, that is, if the rich operation is to be performed, the routine goes to step 63, where the rich air-fuel ratio (A/F)R is calculated. In this embodiment, the rich air-fuel ratio (A/F)R is kept constant at 13.8 regardless the engine operating condition, and thus the rich air-fuel ratio (A/F)R is made 13.8 in step 63. In the following step 64, the rich air-fuel ratio (A/F)R is memorized as the target air-fuel ratio (A/F)T. Next, the routine goes to step 65.

Contrarily, if FRICH is zero, that is, if the lean operation is to be performed, the routine goes to step 66, where the lean air-fuel ratio (A/F)L is calculated. In this embodiment, the lean air-fuel ratio (A/F)L is kept constant at 25.0 regardless the engine operating condition, and thus the lean air-fuel ratio (A/F)L is made 25.0 in step 66. In the following step 67, the lean air-fuel ratio (A/F)L is memorized as the target air-fuel ratio (A/F)T. Next, the routine goes to step 65.

In step 65, the fuel injection time TAU is calculated using the following equation:

$$TAU = TB \cdot ((A/F)S / (A/F)T) \cdot FAF$$

Each fuel injector 5 injects the fuel for the fuel injection time TAU.

Fig. 12 illustrates a routine for executing the control of the ignition timing.

Referring to Fig. 12, first, in step 160, it is judged whether FRICH, which is controlled in the routine shown in Fig. 10, is made zero. If FRICH = 0, that is, if the lean operation is to be performed, the routine goes to step 161, where ITL is calculated in accordance

with, for example, the engine operating condition. In the following step 162, ITL is memorized as the ignition timing IT. Then, the processing cycle is ended.

5 If FRICH = 1 in step 160, that is, if the rich operation is to be performed, the routine goes to step 163, where ITR is calculated in accordance with, for example, ITL. In the following step 164, ITR is memorized as the ignition timing IT. Then, the processing cycle is ended. Each spark plug 15 performs the igniting operation in accordance with the ignition timing ITL or ITR.

10 In the embodiment mentioned above, the exhaust gas can be purified sufficiently using a single exhaust passage, that is, without providing a plurality of the exhaust passages. Accordingly, the structure of the exhaust gas purifying device is kept small and simple.

15 On the other hand, if a ratio of the number of the cylinders which performs the lean engine operation to the number of the cylinders which performs the rich engine operation in one cycle (see Fig. 5) is referred as a cylinder number ratio RATIO, it is desired to make the cylinder number ratio RATIO as large as possible, to thereby make the fuel consumption rate as small as possible. However, if a part of the cylinders performs the rich engine operation and the other performs the lean engine operation as in the prior art device mentioned at the beginning, the cylinder number ratio RATIO is limited. That is, in the four-cylinder engine, for example, the ratio RATIO is limited to 3 and cannot be made larger than 3. Thus, the decrease of the fuel consumption rate is limited, with the identical lean and rich air-fuel ratio (A/F)L and (A/F)R. Contrarily, in the embodiment, the ratio RATIO is allowed to be made larger until the NO_x amount flowing into the NH₃-AO catalyst 10a exceeds the NH₃ amount desorbed from the catalyst 10a. In particular, the cylinder number ratio

RATIO is made larger than 3 in the four-cylinders engine. As a result, the fuel consumption rate is made more lower.

Further, if the first cylinder #1 continuously performs the rich operation and the second, third, and fourth cylinders #2, #3, #4 continuously perform the lean operation, for example, as in the prior art, a large temperature difference between the exhaust gases exhausted from the cylinders #1 to #4 may occur, and may lead a larger temperature drop in the engine body or in the exhaust manifold 7, to thereby lead to a large thermal distortion therein. Furthermore, in this example, a large amount of the deposition may exist in the first cylinder #1 which performs the rich operation continuously. Contrarily, in this embodiment, a cylinder in which the lean or rich operation is to be performed is not specified, that is, every cylinder performs both the lean and the rich operations. Accordingly, a large thermal distortion in the engine body or in the exhaust manifold 7 is prevented, and the large amount of the deposition on the particular cylinder is also prevented.

Additionally, the exhaust gas purifying method according to the present embodiment may be used in a single cylinder engine.

Next, another embodiment for determining the lean and the rich operation period TL, TR, in the engine shown in Fig. 1, will be explained.

In the above-mentioned embodiment, the lean and the rich operation period TL, TR are set in accordance with the adsorbed NH_3 amount $S(\text{NH}_3)$. As a result, the cylinder number ratio RATIO is set in accordance with the adsorbed NH_3 amount $S(\text{NH}_3)$. Contrarily, in this embodiment, a ratio RATIO suitable for purifying NO_x for every engine operating condition is stored in advance, and the lean and the rich operation period TL and TR are set to make the actual cylinder number ratio equal to

this suitable ratio $RATIO$.

In this embodiment, the ratio $RATIO$ is one selected from 1, 2, 3, and 4. Fig. 13 shows the ratio $RATIO$ suitable for purifying NO_x for an engine operating
5 condition defined by the engine load Q/N and the engine speed N . As shown in Fig. 13, the ratio $RATIO$ becomes larger as the engine load Q/N become higher when the engine load Q/N is low, and becomes smaller as the engine load Q/N becomes higher when the engine load Q/N is high,
10 with the constant engine speed N . The ratio $RATIO$ is stored in the ROM 22 in advance in the form of a map as shown in Fig. 13.

For the ratio $RATIO$ obtained from the map shown in Fig. 13, any method can be applied to set the number of
15 the cylinders performing the lean engine operation and that performing the rich engine operation. In this embodiment, the number of the cylinder performing the rich engine operation is set to 1 regardless the ratio $RATIO$. As mentioned above, the ratio $RATIO$ is a ratio of
20 the number of the cylinders performing the lean engine operation to that performing the rich engine operation, in one cycle. Thus, the number of the cylinders performing the lean engine operation is made 1, 2, 3, and 4, for the ratio $RATIO$ 1, 2, 3, and 4, respectively, with
25 the number of cylinder performing the rich engine operation being 1. Next, the method for controlling the engine operation period will be explained in more detail, with reference to Figs. 14 to 17.

In the engine shown in Fig. 1, the combustion stroke
30 of one of the cylinders is in process whenever the crankshaft turns by about 180 degree. That is, the combustion strokes are in process repeatedly in the order of the first #1, the third #3, the fourth #4, and the second cylinder #2. In Figs. 14 to 17, white and black
35 circles represent the lean and the rich engine operations, respectively. Fig. 14 illustrates the case

in which the ratio $RATIO$ is made 1. In this case, the rich operation is performed in one cylinder, that is, for example, the first cylinder #1, and the lean operation is performed in one cylinder, that is, the third cylinder #3. Thus, the rich operation in the first cylinder #1 forms the rich operation period TR , and the lean operation in the third cylinder #3 forms the lean operation period TL , and the operations in the two cylinders form the cycle. The following cycle is formed by the operations of the fourth and the second cylinders #4 and #2.

As mentioned above, in the engine shown in Fig. 1, the combustion stroke is in process whenever the crankshaft turns by about 180 degree, and thus the exhaust stroke periods of the cylinders are different from each other, that is, do not overlap each other. As a result, in the case of $RATIO = 1$, the exhaust gas exhausted from the first cylinder #1 of which exhaust gas air-fuel ratio is rich first flows into the TW catalyst 8a, and then the exhaust gas exhausted from the third cylinder #3 of which exhaust gas air-fuel ratio is lean flows into the TW catalyst 8a, and, in this manner, the exhaust gases from the cylinders flow into the TW catalyst 8a, in turn. Accordingly, the exhaust gas portions of which the exhaust gas air-fuel ratios are rich and lean flow into the TW catalyst 8a alternately and repeatedly. Note that the present invention may be applied in the case in which the exhaust stroke periods slightly overlap to each other.

Fig. 15 shows the case where $RATIO = 2$. In this case, the rich operation is performed in, for example, the first cylinder #1, and the lean operation is performed in two cylinders, that is, the third and the fourth cylinders #3 and #4. Thus, the rich operation in the first cylinder #1 forms the rich operation period TR , and the lean operations in the third and the fourth cylinders #3 and #4 form the lean operation period TL ,

and the operations in the three cylinders form the cycle. The following cycle is formed by the operations of the second, the first, and the third cylinders #2, #1, and #3.

5 Fig. 16 shows the case where $RATIO = 3$. In this case, the rich operation is performed in, for example, the first cylinder #1, and the lean operation is performed in three cylinders, that is, the third, the fourth, and the second cylinders #3, #4, and #2. Thus, 10 the rich operation in the first cylinder #1 forms the rich operation period TR , and the lean operations in the third, the fourth, and the second cylinders #3, #4, and #2 form the lean operation period TL , and the operations in the four cylinders form the cycle. The 15 following cycle is formed by the operation of the first, the third, and the fourth cylinders #1, #3, and #4.

 Fig. 17 shows the case where $RATIO = 4$. In this case, the rich operation is performed in, for example, the first cylinder #1, and the lean operation is 20 performed in four cylinders, that is, the third, the fourth, the second, and the first cylinders #3, #4, #2, and #1. Thus, the rich operation in the first cylinder #1 forms the rich operation period TR , and the lean operations in the third, the fourth, the second, and 25 the first cylinders #3, #4, #2, and #1 form the lean operation period TL , and the operations in the five cylinders form the cycle. The following cycle is formed by the operation of the third, the fourth, the second, the first, and the third cylinders #3, #4, #2, #1, 30 and #3.

 When the ratio $RATIO$ is made equal to or larger than the total number of the cylinders of the engine as in the example shown in Fig. 17, all of the cylinders performs the lean engine operation in one lean operation period. 35 This ensures the longer lean operation period TL , to thereby decrease the fuel consumption rate.

 When setting the cylinder number ratio $RATIO$ to

thereby set the lean and the rich operation periods TL and TR in this way, the NH_3 amount and the NO_x amount flowing into the NH_3 -AO catalyst 10a can be controlled accurate. This results in preventing NO_x and NH_3 from
5 passing through the NH_3 -AO catalyst 10a, and in purifying the exhaust gas sufficiently.

A cylinder performing the rich operation is not fixed when setting the ratio RATIO to thereby set the lean and the rich operation periods TL and TR. Further,
10 a cylinder performing the rich operation varies in every cycle, when the ratio RATIO is made 2 or 4, for example. Thus, the engine body 1 or the exhaust manifold 7 is further prevented from the thermal distortion, and the deposition in the specific cylinder is further prevented.

15 Note that the cylinder performing the rich operation is fixed when the ratio is made 1 or 3, as shown in Fig. 14 or 16. Namely, only the first and the third cylinders #1 and #3 perform the rich operation in the example shown in Fig. 14, and only the first cylinder #1
20 performs the rich operation in the example shown in Fig. 16. However, if the ratio RATIO changes due to the change in the engine operating condition, the cylinder performing the rich operation is changed. Namely, the cylinder performing the rich operation changes whenever
25 the ratio RATIO changes, and thus the cylinder is not necessarily fixed. Note that, if the ratio RATIO is kept identical for a long period due to the stable engine operating condition and thereby a specific cylinder performs the rich operation for a predetermined period,
30 the cylinder performing the rich operation may be changed to the other while keeping the ratio RATIO. Namely, in the example shown in Fig. 16, if the first cylinder #1 performs the rich operation for the predetermined period, the third cylinder #3 performs the rich operation, while
35 the first cylinder performs the lean operation to keep the ratio RATIO, for example. Alternatively, the ratio

RATIO may be changed to 2 or 4 temporarily, to thereby change the cylinder performing the rich operation.

When the lean and the rich operations are performed in accordance with the ratio RATIO, each cylinder is
5 required to be judged whether it has to perform the lean operation or the rich operation. Next, the method for judging whether the cylinder has to perform the lean operation or the rich operation will be explained.

In this embodiment, the product DRICH of the data
10 DRATIO of 5 bits representing the cylinder number ratio RATIO, and the history data DHISTORY of 5 bits representing the engine operations in the last five cylinders is calculated whenever the combustion stroke is in process, and it is judged whether the lean operation
15 or the rich operation is to be performed, on the basis of the product DRICH. The data DRATIO is "00001" for RATIO = 1, "00011" for RATIO = 2, "00111" for RATIO = 3, and "01111" for RATIO = 4, as shown in Fig. 18, and is stored in the ROM 22 in advance in the form of a map as
20 shown in Fig. 18.

The bit in 2^4 of DHISTORY represents the engine operation performed five times before, the bit in 2^3 represents the engine operation performed four times before, the bit in 2^2 represents the engine operation
25 performed three times before, the bit in 2^1 represents the engine operation performed two times before, and the bit in 2^0 represents the last engine operation. In each cylinder, each bit is made zero when the lean operation is performed, and is made 1 when the rich operation is
30 performed. Thus, DHISTORY = "10010", for example, represents that the rich, the lean, the lean, the rich, and the lean operations have been performed, in turn.

The product DRICH of DRATIO and DHISTORY is calculated when the fuel injection time TAU for each
35 cylinder is calculated. The cylinder performs the rich operation when DRICH is "00000", and performs the lean

operation when DRICH is the other. Next, an example of DRICH will be explained with reference to Fig. 19, as well as Fig. 15.

Fig. 19 illustrates the product DRICH in the case in which $RATIO = 2$. In the example shown in Fig. 19, for the second cylinder #2, DHISTORY is "10010" and DRATIO is "00011", and thus DRICH is "00010". As a result, the second cylinder #2 performs the lean operation. That is, the target air-fuel ratio $(A/F)_T$ for the second cylinder #2 is made the lean air-fuel ratio $(A/F)_L$. For the following first cylinder #1, DHISTORY is "00100" and DRATIO is "00011", and thus DRICH is "00000". As a result, the first cylinder #1 performs the rich operation. That is, the target air-fuel ratio $(A/F)_T$ for the first cylinder #1 is made the rich air-fuel ratio $(A/F)_R$. The following third cylinder #3 performs the lean operation because DRICH is "00001", the following fourth cylinder #4 performs the lean operation because DRICH is "00010", and the following second cylinder #2 performs the rich operation because DRICH is "00000".

Fig. 20 shows a routine for executing the embodiment mentioned above. This routine is executed by interruption every predetermined crank angle.

Referring to Fig. 20, first, in step 70, it is judged whether it is in the fuel injection timing of any one of the cylinders. If it is not in the fuel injection timing, the processing cycle is ended. If it is in the fuel injection timing, the routine goes to step 71, where the cylinder number ratio $RATIO$ is calculated using the map shown in Fig. 13. In the following step 72, DRATIO is calculated using the map shown in Fig. 18, on the basis of the ratio $RATIO$ obtained in the step 71. In the following step 73, DRICH is calculated as the product of proposition of DRATIO and DHISTORY. In the following step 74, DHISTORY is renewed on the basis of DRICH in the present processing cycle. In the following step 75, it is judged whether DRICH is "00000". If $DRICH = "00000"$,

WO 97/17532

PCT/JP96/03205

- 37 -

the routine goes to step 76, where FRICH is made 1. FRICH is identical one shown in the routine shown in Fig. 10, and the rich engine operation is performed when FRICH is made 1, as can be seen from the routine shown in Fig. 11. Then, the processing cycle is ended.

5 If DRICH * "00000" in step 75, the routine goes to step 77, where FRICH is made zero. When FRICH is made zero, the lean operation is performed. Then, the processing cycle is ended.

10 In this embodiment, the number of the cylinders performing the rich engine operation in one rich operation period is made 1. As a result, the NH₃ amount flowing into the NH₃-AO catalyst 10a during one rich operation period is made smaller. Therefore, the volume of the NH₃-AO catalyst 10a, as well as the size thereof, can be made very small.

20 Note that, in one cycle, a plurality of cylinders may perform the rich operation. Referring to Fig. 21 which illustrates an example in which the number of the cylinders performing the rich operation in one cycle is made 3, the first, the third, and the fourth cylinders #1, #3, and #4 perform the rich operation, in turn. Then, if the ratio RATIO is made 2, the following six cylinders perform the lean operation. In the following cycle, the third, the fourth, and the second cylinders #3, #4, and #2 perform the rich operation, in turn. In this case, it is prevented that the cylinders performing the rich operation are completely identical to those in the last cycle. That is, the cylinders performing the rich operation vary in every cycle. As a result, in the example shown in Fig. 21, the engine body, for example, is prevented from the thermal distortion, and a large amount of deposition on a specific cylinder is also prevented.

35 In the above-mentioned embodiment, the cylinder number ratio RATIO is set as a function of the engine

WO 97/17532

PCT/JP96/03205

- 38 -

load Q/N and the engine speed N . Alternatively, the ratio $RATIO$ may be set as a function of the intake air amount Q , as shown in Fig. 22. In this case, the ratio $RATIO$ becomes larger as the intake air amount Q becomes larger when Q is small, and becomes smaller as Q becomes larger when Q is large, as shown in Fig. 22.

Next, another method for setting the lean air-fuel ratio $(A/F)L$ will be explained.

During the lean operation in which the engine air-fuel ratio is made the lean air-fuel ratio $(A/F)L$, it is often difficult to ensure the adequate output torque of the engine, and the actual output torque may deviate from the required output torque which is determined in accordance with the engine operating condition, if the target air-fuel ratio $(A/F)T$ is simply made lean. To solve this, in this embodiment, the lean air-fuel ratio $(A/F)L$, which make the actual output torque equal to the required torque in the lean operation, is stored in advance, and the target air-fuel ratio $(A/F)T$ is set to this lean air-fuel ratio $(A/F)L$ in the lean operation.

Fig. 23 shows the lean air-fuel ratio $(A/F)L$ making the actual output torque equal to the required output torque. As shown in Fig. 23, the lean air-fuel ratio $(A/F)L$ is obtained, as a function of the engine load Q/N and the engine speed N , in advance, by experiment. The lean air-fuel ratio $(A/F)L$ becomes larger as the engine load Q/N becomes higher when the engine load Q/N is low, and becomes smaller as the engine load Q/N becomes higher when the engine load Q/N is high, with a constant engine speed N . Further, the lean air-fuel ratio $(A/F)L$ is stored in the ROM 22 in advance in the form of a map of shown in Fig. 23. The lean air-fuel ratio $(A/F)L$ may be calculated using the map shown in Fig. 23, in the step 66 in the routine shown in Fig. 11.

Next, another method for setting the rich air-fuel ratio $(A/F)R$ will be explained.

As mentioned above, shorter rich operation period is

desirable for a lower fuel consumption rate. Thus, it is desired to change the rich air-fuel ratio $(A/F)_R$ in accordance with the engine operating condition, to thereby make the NH_3 amount synthesized in the rich operation period larger. However, if the NH_3 amount flowing into the NH_3 -AO catalyst 10a suddenly increases when the engine air-fuel ratio changes from the lean air-fuel ratio $(A/F)_L$ to the rich air-fuel ratio $(A/F)_R$, the NH_3 may be discharged from the NH_3 -AO catalyst 10a without being adsorbed. Therefore, in this embodiment, the rich air-fuel ratio $(A/F)_R$, which makes the NH_3 amount flowing into the NH_3 -AO catalyst 10a in the rich operation suitable for the decreasing the fuel consumption rate and for good purification of the exhaust gas, is stored in advance, and the target air-fuel ratio $(A/F)_T$ is made equal to the rich air-fuel ratio $(A/F)_R$, in the rich operation.

Fig. 24 shows the rich air-fuel ratio $(A/F)_R$ making the NH_3 amount flowing into the NH_3 -AO catalyst 10a in the rich operation suitable for the decreasing the fuel consumption rate and for good purification of the exhaust gas. As shown in Fig. 24, the rich air-fuel ratio $(A/F)_R$ is stored as a function of the intake air amount Q , in advance, by experiment. The rich air-fuel ratio $(A/F)_R$ is made 14.4 when $Q < Q_1$, becomes smaller as the intake air amount Q becomes larger when $Q_1 < Q < Q_2$, and is made 12.5 when $Q_2 < Q$, where Q_1 and Q_2 are predetermined values. When the intake air amount Q becomes larger and thus the combustion temperature becomes higher, the NO_x amount exhausted from the engine becomes larger suddenly and thus the NH_3 amount flowing into the NH_3 -AO catalyst 10a becomes larger suddenly. Therefore, when the rich air-fuel ratio $(A/F)_R$ is made larger and thereby the combustion temperature is lowered, NH_3 is prevented from excessively flowing into the NH_3 -AO catalyst 10a.

Note that the rich air-fuel ratio (A/F)R is stored in the ROM 22 in advance in the form of the map as shown in Fig. 24. The rich air-fuel ratio (A/F)R may be calculated using the map shown in Fig. 24, in the step 63 in the routine shown in Fig. 11.

Next, a further embodiment for setting the rich air-fuel ratio (A/F)R will be explained with reference to Figs. 25A and 25B.

As mentioned above, the engine shown in Fig. 1 mainly performs the lean operation, and performs the rich operation temporarily. Thus, it is desired that the engine performs the rich operation suitable for the lean operation which is a basic engine operation. In other words, it is desired that the engine performs the rich operation to make the synthesized NH_3 amount thereby equal to that suitable for purifying NO_x flowing into the NH_3 -AO catalyst 10a in the lean operation. Therefore, in this embodiment, a changing value DROP in the target air-fuel ratio (A/F)T making the rich operation suitable for the last lean operation is stored in advance, and the rich air-fuel ratio (A/F)R is calculated by subtracting the changing value DROP from the lean air-fuel ratio (A/F)L in the last lean operation, as shown in Fig. 25A. The changing value DROP varies in accordance with the engine operating condition, and is thus set in accordance with the engine operating condition just before the rich operation in question starts, such as an engine load. This results in purifying the exhaust gas sufficiently, regardless the lean air-fuel ratio (A/F)L.

Fig. 25B shows the changing value DROP obtained in advance by experiment. As shown in Fig. 25B, the changing value DROP becomes smaller as the engine load Q/N becomes higher, and is stored in the ROM 22 in advance in the form of a map as shown in Fig. 25B. In the step 63 in the routine shown in Fig 11, first the changing value DROP may be calculated using the map shown

in Fig. 25B, and then the rich air-fuel ratio $(A/F)R$ may be calculated by subtracting DROP from the lean air-fuel ratio $(A/F)L$ calculated in the step 66.

5 Alternatively, the rich air-fuel ratio $(A/F)R$ may be a standard value, and the lean air-fuel ratio $(A/F)L$ may be calculated by adding a changing value to the rich air-fuel ratio $(A/F)R$, to thereby make the lean operation suitable for the last rich operation.

10 Next, another embodiment for controlling the target air-fuel ratio $(A/F)T$ for each cylinder will be explained with reference to Figs. 26 to 30.

15 In the above-mentioned embodiments, the target air-fuel ratio $(A/F)T$ of the cylinders is made the lean and the rich air-fuel ratios $(A/F)L$ and $(A/F)R$ alternately and repeatedly to make the exhaust air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean and rich alternately and repeatedly, as shown in Fig. 5. Also, in the above-mentioned embodiments, the target air-fuel ratio is changed in the form of the step.
20 However, if the target air-fuel ratio is changed in the form of the step, there may occur a drastic change in the output torque of the engine, which is undesirable, and the drivability may deteriorate. Thus, in this embodiment, as shown in Fig. 26, the target air-fuel ratio $(A/F)T$ is made smaller from the lean air-fuel ratio $(A/F)L$ such as 25.0 to the rich air-fuel ratio $(A/F)R$ such as 13.8 gradually with a predetermined changing rate SLOPER, and is made larger from the rich air-fuel ratio $(A/F)R$ to the lean air-fuel ratio $(A/F)L$ with a
25 predetermined changing rate SLOPEL. The rates SLOPER and SLOPEL are set in accordance with the engine operating condition, respectively. This prevents a drastic change in the output torque, and ensures the good drivability.

30 In the embodiment shown in Fig. 27, the target air-fuel ratio $(A/F)T$ is also made smaller gradually with the changing rate SLOPER, and is also made larger gradually with the changing rate SLOPEL. This ensures good
35

drivability. Further, in this embodiment, the target air-fuel ratio (A/F)_T is kept constant at the lean air-fuel ratio (A/F)_L, for a predetermined period, after the target air-fuel ratio (A/F)_T reaches the lean
 5 air-fuel ratio (A/F)_L, and then is made smaller with the rate SLOPER toward the rich air-fuel ratio (A/F)_R. As a result, the lean operation period TL is made longer than that in the embodiment shown in Fig. 26, and the fuel consumption rate is made further smaller. Additionally,
 10 the changing operation of the target air-fuel ratio (A/F)_T between the lean and the rich air-fuel ratios per unit time is made smaller, and thereby the drivability is further enhanced.

As mentioned above, the TW catalyst 8a synthesizes
 15 NH₃ for purifying NO_x in the rich operation. However, if the target air-fuel ratio (A/F)_T is made smaller gradually from the lean air-fuel ratio (A/F)_L to the rich air-fuel ratio (A/F)_R, the NH₃ amount synthesized in the TW catalyst 8a may not increase quickly, or the NH₃-AO
 20 catalyst 10a may desorb NH₃ excessive to NO_x flowing into the catalyst 10a. Thus, in the embodiment shown in Fig. 28, the target air-fuel ratio (A/F)_T is changed from the lean air-fuel ratio to the rich air-fuel ratio quickly in the form of the step, to thereby prevent NH₃,
 25 and NO_x from being discharged without being purified. Note that the target air-fuel ratio (A/F)_T is changed from the rich air-fuel ratio to the lean air-fuel ratio gradually with the rate SLOPEL, to thereby suppress the undesired fluctuation of the output torque.

In the embodiment shown in Fig. 29, the target air-fuel ratio (A/F)_T is made smaller gradually with the rate SLOPER, and is made larger gradually with the rate SLOPEL, as shown in, for example, Fig. 26. However, in this embodiment, the absolute value SLOPER is made
 30 smaller than that of SLOPEL, and thus the fluctuation of the output torque is suppressed, while preventing the NH₃,
 35

amount from being too small to purify NO_x .

Further, in the embodiment shown in Fig. 29, the target air-fuel ratio $(A/F)_T$ is kept constant at the lean air-fuel ratio $(A/F)_L$ for a predetermined period, after
5 the target air-fuel ratio $(A/F)_T$ is made equal to the lean air-fuel ratio $(A/F)_L$, and then is made smaller toward the rich air-fuel ratio $(A/F)_R$. The target air-fuel ratio $(A/F)_T$ is kept constant at the rich air-fuel ratio $(A/F)_R$ for a predetermined period, after
10 the target air-fuel ratio $(A/F)_T$ is made equal to the rich air-fuel ratio $(A/F)_R$, and then is made larger toward the lean air-fuel ratio $(A/F)_L$. As a result, the changing operation of the target air-fuel ratio $(A/F)_T$ between the lean and the rich air-fuel ratios per unit
15 time is made smaller, and thereby the drivability is further enhanced.

In the embodiments shown in Figs. 26 to 29, while the changing rate SLOPE_L , SLOPE_R may be set constant regardless the engine operating condition, the rate
20 SLOPE_L , SLOPE_R may be set in accordance with the engine operating condition. Fig. 30 shows relationships between the rates SLOPE_L and SLOPE_R and the engine load Q/N . As shown in Fig. 30, each rate SLOPE_L , SLOPE_R becomes smaller as the engine load Q/N becomes higher. The rates
25 SLOPE_L and SLOPE_R are stored in the ROM 22 in advance in the form of a map shown in Fig. 30.

Further, in the embodiments shown in Figs. 26 to 29, the changing rates SLOPE_L and SLOPE_R are kept constant through one changing process of the target air-fuel ratio
30 $(A/F)_T$ between the lean and the rich air-fuel ratios. Alternatively, the changing rates SLOPE_L and SLOPE_R may be changed in one changing process of the target air-fuel ratio $(A/F)_T$, in accordance with, for example, the engine operating condition.

35 On the other hand, the ignition timing for each cylinder is changed gradually in accordance with the

change in the target air-fuel ratio $(A/F)_T$, when the target air-fuel ratio $(A/F)_T$ is changed as in the embodiments mentioned above. Namely, in the embodiment shown in Fig. 26, for example, the ignition timing IT is
5 retarded gradually with a changing rate SR when the target air-fuel ratio $(A/F)_T$ is made smaller gradually, and is advanced gradually with a changing rate SL when the target air-fuel ratio $(A/F)_T$ is made larger gradually. The rates SL and SR corresponds to the rates
10 SLOPEL and SLOPER, respectively. This suppresses the undesired fluctuation in the output torque more effectively. Note that the rates SL and SR may be kept constant, or may be changed in accordance with the engine operating condition.

15 Fig. 31 shows a routine for controlling the ignition timing in the embodiment shown in Fig. 26. This routine is executed by interruption every predetermined crank angle.

Referring to Fig. 31, first, in step 170, it is
20 judged whether FRICH, which is made zero or 1 in the routine shown in Fig. 10, is made 1. If $FRICH = 0$, that is, if the engine has to perform the lean operation, the routine goes to step 171, where the ignition timing IT is increased by SL, namely, is advanced by SL. In the
25 following step 172, ITL is calculated in accordance with the engine operating condition, for example. In the following step 173, it is judged whether the ignition timing IT is larger than ITL. If $IT > ITL$, the routine goes to step 174, where the ignition timing IT is limited
30 to ITL. Then, the processing cycle is ended.

If $FRICH = 1$ in step 170, that is, if the engine has to perform the rich operation, the routine goes to step 175, where the ignition timing IT is decreased by SR, namely, is retarded by SR. In the following
35 step 176, ITR is calculated in accordance with, for example, the engine operation. In the following step 177, it is judged whether the ignition timing IT is

smaller than ITR. If $IT < ITR$, the routine goes to step 178, where the ignition timing IT is limited to ITR. Then, the processing cycle is ended.

Fig. 32 shows another embodiment for the engine according to the present invention. In Fig. 32, constituent elements the same as those in Fig. 1 are given the same reference numerals. The engine is provided with an electronic control unit same as shown in Fig. 1, but it is not depicted in Fig. 32.

Referring to Fig. 32, the engine body 1 is provided with a first bank 1a arranged in one side of the crank shaft (not shown), and a second bank 1b arranged in the other side of the crank shaft. The first bank 1a comprises the first, the third, the fifth, and the seventh cylinders #1, #3, #5, and #7 aligned straight, and the second bank 1b comprises the second, the fourth, the sixth, and the eighth cylinders #2, #4, #6, and #8 aligned straight. Connected to the cylinders of the first bank 1a is a common exhaust manifold 7a, and connected to the cylinders of the second bank 1b is a common exhaust manifold 7b. The exhaust manifolds 7a and 7b are connected to the common TW catalyst 8a via corresponding exhaust pipes 80a, 80b. Note that the upstream side air-fuel ratio sensor 29a is arranged in the exhaust passage downstream of the portion meeting the exhaust pipes 80a and 80b, in this embodiment. Alternatively, the upstream side sensor 29a may comprise a pair of sensors, one being arranged in the manifold 7a, and the other being arranged in the manifold 7b.

This engine also performs the lean and the rich engine operations alternately and repeatedly, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean and rich alternately and repeatedly, as shown in Fig. 5. Namely, the engine performs the rich operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a rich, to thereby synthesize

NH₃ and adsorbed NH₃ in the NH₃-AO catalyst 10a, and performs the lean operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean, to thereby desorb NH₃ and
5 reduce NO_x by the desorbed NH₃ in the NH₃-AO catalyst 10a.

In this engine, the lean and the rich operation period may be set on the basis of the cylinder number ratio RATIO, as explained with reference to Figs. 13 to 21. In this case, the ratio RATIO is selected from 1 to
10 7. In the multi-cylinder engine with 8 or more cylinders, as shown in Fig 32, the ratio RATIO can be set larger such as 5, 6, and 7, and thus the fuel consumption rate is made lower than that in the engine shown in Fig. 1.

15 In the engine shown in Fig. 32, the exhaust stroke is in process, in the order of the first, the eighth, the fourth, the third, the sixth, the fifth, the seventh, and the second cylinders, whenever the crank shaft turns by about 90 degrees. In this case, the beginning of the
20 exhaust stroke period of a certain cylinder overlaps the end of that of the preceding cylinder, and the end of the exhaust stroke period of that certain cylinder overlaps the beginning of that of the following cylinder. However, when the engine performs the lean and the rich
25 operations alternately and repeatedly, the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a is made lean and rich alternately and repeatedly. Thus, even though the exhaust stroke period overlaps that of the other cylinder, the exhaust
30 gas can be purified sufficiently. The other constructions of the exhaust purifying device and the operation thereof are the same as those in the engine shown in Fig. 1, and thus the explanations therefor are omitted.

35 Next, another embodiment for the engine shown in Fig. 32 will be explained.

In this embodiment, the engine 1 is provided with four cylinder groups, that is, a first group having the first and the second cylinders, a second group having the third and the fourth cylinders, a third group having the fifth and the sixth cylinders, a fourth group having the seventh and the eighth cylinders. The exhaust stroke periods of the cylinders in the same cylinder groups are substantially identical to each other, but the exhaust stroke periods of the groups are different from each other. Namely, the exhaust strokes are in process whenever the crank shaft turns by about 90 degrees, in the order of the first, the third, the fourth, and the second cylinder groups.

This engine also performs the lean and the rich engine operations alternately and repeatedly, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean and rich alternately and repeatedly, as shown in Fig. 5. Namely, the engine performs the rich operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a rich, to thereby synthesize NH_3 and adsorbed NH_3 in the NH_3 -AO catalyst 10a, and performs the lean operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10a lean, to thereby desorb NH_3 and reduce NO_x by the desorbed NH_3 on the NH_3 -AO catalyst 10a.

In this engine, to make the exhaust gas air-fuel ratio of the exhaust gas exhausted from the first cylinder group, for example, equal to the target air-fuel ratio $(A/F)_T$, any method may be applied to set the engine air-fuel ratios of the first and the second cylinders #1 and #2. In the embodiment, the engine air-fuel ratios of the first and the second cylinders #1 and #2 are set identical to each other and are made equal to the target air-fuel ratio $(A/F)_T$. However, the important point is that making the exhaust gas air-fuel ratio of the exhaust

gas flowing into the catalysts 8a and 10a equal to the target air-fuel ratio (A/F)_T, and making both of the engine air-fuel ratios of the first and the second cylinders equal to the target air-fuel ratio (A/F)_T is unnecessary. The above explanation may be applied to the other cylinder groups, and thus particular explanations therefor are omitted.

In this engine, the lean and the rich operation period may also be set on the basis of the cylinder number ratio *RATIO*, as explained with reference to Figs. 13 to 21. In this case, the ratio *RATIO* may be considered as a ratio of the number of the cylinder groups performing the lean operation to the number of the cylinder groups performing the rich operation, in one cycle. Further, note that each cylinder group may have a single cylinder. The other constructions of the exhaust purifying device and the operation thereof are the same as those in the engine shown in Fig. 1, and thus the explanations therefor are omitted.

Next, another embodiment for the engine shown in Fig. 33 will be explained. In Fig. 33, constituent elements the same as those in Fig. 1 are given the same reference numerals.

Referring to Fig. 33, the exhaust gas purifying catalyst 10 is housed in the catalytic converter 9 in which the TW catalyst 8a is housed. Especially, the exhaust gas purifying catalyst 10 is carried on the substrate carrying the TW catalyst 8a, and is arranged downstream of the TW catalyst 8a, in series, as shown in Fig. 33. Additionally, the NH₃ purifying catalyst 12 is arranged downstream of the exhaust gas purifying catalyst 10, as in the engine shown in Fig. 1.

In the engine shown in Fig. 33, the exhaust gas purifying catalyst 10 consists of a NO_x occluding and reducing catalyst 10b, which is simply expressed as a NO_x-OR catalyst. The NO_x-OR catalyst 10b comprises at

least one substance selected from alkali metals such as potassium K, sodium Na, lithium Li, and cesium Cs, alkali earth metals such as barium Ba and calcium Ca, rare earth metals such as lanthanum La and yttrium Y, and transition
5 metals such as iron Fe and copper Cu, and of precious metals such as palladium Pd, platinum Pt, and rhodium Rh, which are carried on alumina as a carrier. The NO_x-OR catalyst 10b performs the NO_x occluding and releasing
10 function in which it occludes NO_x therein when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, and releases the occluded NO_x therefrom when the oxygen concentration in the inflowing exhaust gas becomes lower.

When the NO_x-OR catalyst 10b is disposed in the
15 exhaust passage of the engine, the NO_x-OR catalyst 10b actually performs the NO_x occluding and releasing function, but the function is unclear. However, it can be considered that the function is performed according to the mechanism as shown in Fig. 34. This mechanism will
20 be explained by using as an example a case where platinum Pt and barium Ba are carried on the carrier, but a similar mechanism is obtained even if another precious metal, alkali metal, alkali earth metal, or rare earth metal is used.

25 Namely, when the exhaust gas air-fuel ratio of the inflowing exhaust gas becomes lean, that is, when the oxygen concentration in the inflowing exhaust gas increases, the oxygen O₂ is deposited on the surface of platinum Pt in the form of O₂ or O²⁻, as shown in
30 Fig. 34A. On the other hand, NO in the inflowing exhaust gas reacts with the O₂ or O²⁻ on the surface of the platinum Pt and becomes NO₂ (2NO + O₂ → 2NO₂). Subsequently, a part of the produced NO₂ is oxidized on the platinum Pt and is occluded into the NO_x-OR
35 catalyst 10b. While bonding with barium oxide BaO, it is

diffused in the catalyst 10b in the form of nitric acid ions NO_3^- , as shown in Fig. 34A. In this way, NO_x is occluded in the NO_x -OR catalyst 10b.

Contrarily, when the oxygen concentration in the inflowing exhaust gas becomes lower and the production of NO_2 is lowered, the reaction proceeds in an inverse direction ($\text{NO}_3^- \rightarrow \text{NO}_2$), and thus nitric acid ions NO_3^- in the NO_x -OR catalyst 10b is released in the form of NO_2 from the NO_x -OR catalyst 10b, as shown in Fig. 34B.

Namely, when the oxygen concentration in the inflowing exhaust gas is lowered, that is, when the exhaust gas air-fuel ratio of the inflowing exhaust gas is changed lean to rich, NO_x is released from the NO_x -OR catalyst 10b. At this time, if the reducing agent, such as NH_3 , exists in the NO_x -OR catalyst 10b, NO_x is reduced and purified by the agent. Note that, when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, hydrocarbon HC, carbon monoxide CO, or hydrogen H_2 may pass through the TW catalyst 8a and may flow into the NO_x -OR catalyst 10b. It is considered that the HC, CO, etc. act as the reducing agent, as well as NH_3 , and reduce a part of NO_x on the NO_x -OR catalyst 10b.

However, the reducing ability of NH_3 is higher than those of HC, CO, etc., and thus NO_x can be reliably purified by using NH_3 as the reducing agent.

This engine also performs the lean and the rich engine operations alternately and repeatedly, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10b lean and rich alternately and repeatedly, as shown in Fig. 38B. When the engine performs the lean operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10b lean, NO_x in the exhaust gas passes through the TW catalyst 8a, and then flows into the NO_x -OR catalyst 10b, as shown in Fig. 35B. At

this time, the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, and thus NO_x in the inflowing exhaust gas is occluded in the NO_x -OR catalyst 10b.

5 On the other hand, when the engine performs the rich operation to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10b rich, a part of the NO_x is converted to NH_3 on the TW catalyst 8a, as shown in Fig. 35A. The NH_3 then flows
10 into the NO_x -OR catalyst 10b. At this time, the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, and thus the occluded NO_x is released from the NO_x -OR catalyst 10b. The released NO_x is reduced by the NH_3 in the inflowing exhaust gas, and is thus purified. Note
15 that, even if the NH_3 amount inflowing the NO_x -OR catalyst 10b exceeds an amount required for purifying the released NO_x , the excess NH_3 flows into the NH_3 purifying catalyst 12, and is purified there. This prevents NH_3 from being emitted to the ambient air. Further, the lean
20 and the rich air-fuel ratio (A/F)L and (A/F)R are also set to 25.0 and 13.8, respectively, in this engine.

Next, the method for controlling the lean and the rich operation periods in the engine shown in Fig. 33 will be explained.

25 It is desirable that the lean operation period TL is made longer, as in the engine shown in Fig. 1, but the NO_x -OR catalyst 10b will saturate with NO_x if the lean operation is made too long. On the other hand, if the rich operation is made too short, the target air-fuel
30 ratio (A/F)T has to be changed between the lean and the rich air-fuel ratios frequently. Thus, in this embodiment, the NO_x amount occluded in the NO_x -OR catalyst 10b is obtained, and the engine performs the rich operation when the occluded NO_x amount exceeds a
35 predetermined maximum amount in the lean operation, and

performs the lean operation when the occluded NO_x amount falls below a predetermined minimum amount in the rich operation.

It is difficult to directly find the occluded NO_x amount in the NO_x -OR catalyst 10b. Therefore, in this embodiment, the occluded NO_x amount is estimated on the basis of the NO_x amount flowing into the NO_x -OR catalyst 10b, that is, the NO_x amount exhausted from the engine. Namely, the exhausted NO_x amount per unit time $Q(\text{NO}_x)$ is calculated using the map shown in Fig. 6.

Fig. 36A illustrates the NO_x amount $D(\text{NO}_x)$ released from the NO_x -OR catalyst 10b per unit time, obtained by experiments. In Fig. 36A, the solid curve shows the case where the temperature of the NO_x -OR catalyst 10b is high, and the broken curve shows the case where the temperature of the NO_x -OR catalyst 10b is low. Further, in Fig. 36A, TIME represents a time starting from when the rich operation starts, that is, when the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a and 10b is changed from the lean air-fuel ratio $(A/F)_L$ to the rich air-fuel ratio $(A/F)_R$. The decomposition rate of NO_x in the NO_x -OR catalyst 10b becomes higher as the temperature of the catalyst 10b becomes higher. Thus, when the temperature of the NO_x -OR catalyst 10b, that is, the temperature of the exhaust gas flowing into the catalyst 10b TNC, is high, as shown by the solid line in Fig. 36A, a large amount of NO_x is released from the NO_x -OR catalyst 10b in a short time, while when TNC is low as shown by the broken line in Fig. 36A, a small amount of NO_x is released. In other words, the released NO_x amount per unit time $D(\text{NO}_x)$ becomes larger as the exhaust gas temperature TNC becomes higher. The released NO_x amount $D(\text{NO}_x)$ is stored in the ROM 22 in advance in the form of a map as shown in Fig. 36B.

While the exhaust gas temperature TNC may be

detected by using a temperature sensor arranged in the exhaust passage, TNC is estimated on the basis of the engine load Q/N and the engine speed N, in this embodiment. That is, TNC is obtained in advance by experiment and is stored in the ROM 22 in advance in the form of a map as shown in Fig. 37.

Next, the method for controlling the operation period for the engine shown in Fig. 33 will be explained in more detail, with reference to Figs. 38A and 38B. The routine shown in Fig. 38A is executed by interruption every predetermined crank angle.

Referring to Fig. 38A, first, in step 80, it is judged whether FRICH is made 1. FRICH is made 1 when the rich operation is to be performed, and is made zero when the lean operation is to be performed. If FRICH is 1, that is, if the rich operation is to be performed, the routine goes to step 81, where the exhaust gas temperature TNC is calculated using the map shown in Fig. 37. In the following step 82, D(NO_x) is calculated using the map shown in Fig. 36B. In the following step 83, the NO_x amount S(NO_x) occluded in the NO_x-OR catalyst 10b is calculated using the following equation:

$$S(\text{NO}_x) = S(\text{NO}_x) - D(\text{NO}_x) \cdot \text{DELTA}d$$

where DELTAd is a time interval from the last processing cycle until the present processing cycle. In the following step 84, it is judged whether the occluded NO_x amount S(NO_x) is smaller than the minimum amount MIN(NO_x). If S(NO_x) ≥ MIN(NO_x), the processing cycle is ended. Namely, if S(NO_x) ≥ MIN(NO_x), it is judged that the occluded NO_x amount S(NO_x) is still large, and thus the rich operation is continued.

If S(NO_x) < MIN(NO_x), the routine goes to step 85, where FRICH is made zero and the processing cycle is ended. Namely, if S(NO_x) < MIN(NO_x), it is judged that the NO_x-OR catalyst 10b cannot release NO_x sufficient for

the NH_3 flowing therein, and thus the rich operation is stopped and the lean engine operation starts (as at the time a, c, e, or g shown in Fig. 38B).

Contrarily, if $\text{FRICH} = 0$ in step 80, that is, if the lean operation is to be performed, the routine goes to step 86, where the exhausted NO_x amount $Q(\text{NO}_x)$ is calculated using the map shown in Fig. 6B. In the following step 87, the occluded NO_x amount $S(\text{NO}_x)$ is calculated using the following equation:

$$S(\text{NO}_x) = S(\text{NO}_x) + Q(\text{NO}_x) \cdot \text{DELTAa}$$

where DELTAa is a time interval from the last processing cycle until the present processing cycle. In the following step 88, it is judged whether the occluded NO_x amount $S(\text{NO}_x)$ is larger than the maximum amount $\text{MAX}(\text{NO}_x)$, which is determined in accordance with the occluding capacity of the catalyst 10b. If $S(\text{NO}_x) \leq \text{MAX}(\text{NO}_x)$, the processing cycle is ended. Namely, if $S(\text{NO}_x) \leq \text{MAX}(\text{NO}_x)$, the occluded NO_x amount is judged to be small, and thus the lean operation is continuously performed.

If $S(\text{NO}_x) > \text{MAX}(\text{NO}_x)$, the routine goes to step 89, where FRICH is made 1, and then the processing cycle is ended. Namely, if $S(\text{NO}_x) > \text{MAX}(\text{NO}_x)$, the occluded NO_x amount is considerably large, and the lean operation is stopped and the rich operation starts (as at the time b, d, or f shown in Fig. 38B).

Also, in this embodiment, the exhaust gas can be purified sufficiently without providing a plurality of the exhaust passages. Accordingly, the structure of the exhaust passage is kept small and simple. The other constructions of the exhaust purifying device and the operation thereof are the same as those in the engine shown in Fig. 1, and thus the explanations therefor are omitted.

Next, a further embodiment will be explained with reference to Fig. 39. In Fig. 39, constituent elements

the same as those in Fig. 1 are given the same reference numerals.

Referring to Fig. 39, the exhaust gas purifying catalyst 10 comprises both of the NH_3 -AO catalyst 10a and the NO_x -OR catalyst 10b. The NO_x -OR catalyst 10b is carried on the carrier common to the TW catalyst 8a, and the NH_3 -AO catalyst 10a is arranged in the muffler 11 downstream of the NO_x -OR catalyst 10b. Further, the NH_3 purifying catalyst 12 is arranged downstream of the NH_3 -AO catalyst 10a.

In this engine again, the target air-fuel ratio (A/F)_T of the cylinders is made equal to the lean and the rich air-fuel ratios (A/F)_L and (A/F)_R alternately and repeatedly, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a lean and rich alternately and repeatedly. In this embodiment, the purification of the exhaust gas is performed mainly by the NO_x -OR catalyst 10b, arranged on the upstream side, and the NH_3 -AO catalyst 10a is auxiliary. Namely, when the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is made lean, as shown in Fig. 40B, NO_x exhausted from the engine passes through the TW catalyst 8a, and then flows into the NO_x -OR catalyst 10b. At this time, the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, and thus NO_x is occluded in the NO_x -OR catalyst 10b. Even if the NO_x passes through the NO_x -OR catalyst 10b without being occluded, the NO_x is purified in the following NH_3 -AO catalyst 10a. Namely, at this time, the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean and thus NH_3 is desorbed therefrom, and thereby this NH_3 reduces NO_x . Note that, when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, NH_3 is desorbed from the NH_3 -AO catalyst 10a regardless the NO_x amount flowing therein. However, the

excess NH_3 is purified in the following catalyst 12. Accordingly, NO_x and NH_3 both are prevented from being emitted to the ambient air.

5 When the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is made rich, as shown in Fig. 40A, NO_x exhausted from the engine flows into the TW catalyst 8a, and a part thereof is converted to NH_3 . The NH_3 then flows into the NO_x -OR catalyst 10b. At this time, the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, NO_x is released from the NO_x -OR catalyst 10b. The NO_x is reduced and purified by the inflowing NH_3 . Even if NH_3 passes through the NO_x -OR catalyst 10b without reducing NO_x , the NH_3 is adsorbed in the NH_3 -AO catalyst 10a. 10 Further, even if NH_3 passes through the NH_3 -AO catalyst 10a without being adsorbed therein, the NH_3 is purified in the catalyst 12. Accordingly, NO_x and NH_3 both are purified sufficiently. 15

In this embodiment, the lean and the rich operation periods TL and TR are set in accordance with the occluded NO_x amount in the NO_x -OR catalyst 10b, as in the engine shown in Fig. 33. Namely, the lean operation is stopped and the rich operation starts when the occluded NO_x amount exceeds over the maximum amount, and the rich operation is stopped and the lean operation starts when the occluded NO_x amount falls below the minimum amount. However, if the occluded NO_x amount exceeds the maximum amount and the catalyst 10b saturates, NO_x passing through the catalyst 10b then flows into the NH_3 -AO catalyst 10a and is reduced by NH_3 desorbed therefrom. Accordingly, precise control of the operation period is unnecessary for purifying NO_x sufficiently. 20 25 30

Alternatively, the lean and the rich operation periods TL and TR may be set in accordance with the NH_3

amount adsorbed in the NH_3 -AO catalyst 10a, as in the engine shown in Fig. 1. Further alternatively, the lean and the rich operation periods TL and TR may be set in the manner that the lean operation is stopped and the rich operation starts when the occluded NO_x amount in the NO_x -OR catalyst 10b exceeds the maximum amount therefor, and the rich operation is stopped and the lean operation starts when the adsorbed NH_3 amount in the NH_3 -AO catalyst 10a exceeds the maximum amount therefor.

Further alternatively, the rich operation may start when the adsorbed NH_3 amount in the NH_3 -AO catalyst 10a falls below the minimum amount therefor during the lean operation, and lean operation may start when the occluded NO_x amount in the NO_x -OR catalyst 10b falls below the minimum amount therefor during the rich operation. In this alternative, setting the minimum amounts for the catalysts 10a and 10b relatively large results in that NH_3 is always adsorbed in the NH_3 -AO catalyst 10a and NO_x is always occluded in the NO_x -OR catalyst 10b. Thus, even though the actual engine air-fuel ratio deviates from the target air-fuel ratio $(A/F)_T$ due to the engine transient operation, the exhaust gas is purified sufficiently by at least one of the catalysts 10a and 10b. Accordingly, the exhaust gas is purified regardless the engine operation condition.

In this way, the engine shown in Fig. 39 also purifies the exhaust gas with a single exhaust passage.

In the embodiment shown in Fig. 39, the NO_x -OR catalyst 10b is arranged on the upstream side, and the NH_3 -AO catalyst 10a is arranged on the downstream side, considering the endurance temperatures of the catalysts 10a and 10b. Alternatively, the NH_3 -AO catalyst 10a may be arranged on the upstream side, and the NO_x -OR catalyst 10b is arranged on the downstream side. In this alternative, setting the lean and the rich

operation periods in accordance with the adsorbed NH_3 amount in the NH_3 -AO catalyst 10a makes the controllability easier. Further alternatively, the catalysts 10a and 10b may be arranged in parallel. The other constructions of the exhaust purifying device and the operation thereof are the same as those in the engine shown in Fig. 1, and thus the explanations therefor are omitted.

Figs. 41A and 41B illustrate another embodiment for the arrangement of the exhaust gas purifying catalyst 10.

Referring to Figs. 41A and 41B, the NH_3 -AO catalyst 10a and the NO_x -OR catalyst 10b are carried on a common substrate, while they are carried on the individual substrates in the embodiment shown in Fig. 39. Namely, in the embodiment shown in Fig. 41A, the catalysts 10a and 10b are laminated to each other and carried on a common substrate 110. As shown in Fig. 41A, a layer comprised of the NH_3 -AO catalyst 10a is first formed over the surface of the substrate 110 having a honeycomb structure, and then a layer comprised of the NO_x -OR catalyst 10b is formed over the NH_3 -AO catalyst 10a. As mentioned above, the endurance temperature of the NO_x -OR catalyst 10b is higher than that of the NH_3 -AO catalyst 10a. Therefore, covering the NH_3 -AO catalyst 10a by the NO_x -OR catalyst 10b prevents the direct contact of the exhaust gas with the NH_3 -AO catalyst 10a. As a result, good purification of the exhaust gas is ensured, while ensuring the endurance of the NH_3 -AO catalyst 10a.

On the other hand, in the embodiment shown in Fig. 41B a layer 10c is carried on the substrate 110. The layer includes the catalysts 10a and 10b in a mixed form. In this case, for example, the NH_3 -AO catalysts 10a are comprised of zeolite carrying the metal thereon by the ion changing process, and the NO_x -OR

catalyst 10b is comprised of alumina carrying the precious metal and the alkali metal or alkali earth metal or the like. These catalysts 10a and 10b are mixed and then applied over the surface of the substrate 110.

5 This way of carrying the catalysts 10a and 10b makes the structure of the exhaust gas purifying device simpler.

10 Next, another embodiment will be explained with reference to Fig. 42. In Fig. 42, constituent elements the same as those in Fig. 1 are given the same reference numerals. Also, in Fig. 42, the exhaust gas purifying catalyst 10 comprises both the NH_3 -AO catalyst 10a and the NO_x -OR catalyst 10b, but one of them may be omitted.

15 Referring to Fig. 42, there is provided a making rich device 120 for making the exhaust gas air-fuel ratio of the exhaust gas, flowing into the catalysts 8a, 10a, and 10b, rich. In this embodiment, the device 120 comprises an auxiliary internal combustion engine 120a, of which a crank shaft is different from that of the
20 engine 1. Arranged in an intake duct 124 of the auxiliary engine 120a is a fuel injector 125 for feeding fuel such as gasoline to the auxiliary engine 120a. In the intake duct 124 upstream of the injector 125, a throttle valve 126 is also arranged. On the other hand,
25 an exhaust pipe 127 of the auxiliary engine 1 is connected to an interconnecting pipe 129 connecting both of the exhaust manifold 7 and exhaust pipe 127 to the catalytic converter 9 in which the TW catalyst 8a is housed. Thus, the exhaust gas flowing into, in turn, the
30 catalysts 8a, 10b, 10a, and 12 is a mixture of the exhaust gas from the engine 1 and that from the auxiliary engine 120a. Note that, while the auxiliary engine 120a shown in Fig. 42 is constructed as an spark-ignition type engine having a single cylinder, the auxiliary
35 engine 120a may be constructed as a multi-cylinder engine, or a diesel engine.

Mounted in the intake duct 124 is a pressure sensor 137 generating an output voltage proportional to a pressure in the intake duct 124. The output voltage of the sensor 137 is input via an AD converter 138 to the input port 25. The intake air amount AQ of the auxiliary engine 120a is calculated in the CPU 24 on the basis of the output signals from the AD converter 138. Further, mounted in the collecting portion of the exhaust manifold 7 is an upstream side air-fuel ratio sensor 29c generating an output voltage proportional to an exhaust gas air-fuel ratio of the exhaust gas flowing through the collecting portion of the exhaust manifold 7. The output voltage of the sensor 29c is input via an AD converter 30c to the input port 25. The air-fuel ratio sensor 29a is mounted in the interconnecting pipe 129 downstream on the meeting point where the exhaust gases from the exhaust manifold 7 and the exhaust pipe 127 meet with each other. Thus, the sensor 29a generates an output voltage proportional to the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a. Further, connected to the input port 25 is a crank angle sensor 131 generating an output pulse whenever the crank shaft of the auxiliary engine 120a turns by, for example, 30 degrees. The CPU 24 calculates the engine speed AN of the auxiliary engine 120a in accordance with the pulse. Further, arranged in the interconnecting pipe 129 downstream of the meeting point mentioned above is a temperature sensor 140 generating an output voltage proportional to the temperature of the exhaust gas flowing into the catalysts 8a, 10b, and 10a, which represents the temperature of the catalysts 8a and 10b. The output port 26 is connected to the fuel injector 125 via a corresponding drive circuit 32.

The output torque of the engine 1 is used for driving the automobile, for example. Contrarily, the output torque of the auxiliary engine 120a is used for driving an auxiliary device 132, such as a cooling device

for an insulated van, a mixer for a concrete mixer truck,
an air-conditioner for a bus, and an electric generator
for generating the electric power for the electrical
motor of the so-called hybrid type vehicle which is
5 driven by the engine and the electrical motor. The
throttle valve 126 of the auxiliary engine 120a is
controlled in accordance with the required output torque
of the auxiliary engine 120a. Alternatively, the
auxiliary device 132 may be an auxiliary machinery of the
10 engine 1 such as a cooling water pump, an oil pump, and
an alternator.

In this embodiment, basically, the engine 1 performs
the lean operation continuously with the lean air-fuel
ratio (A/F)_L such as 25.0, as shown in Fig. 43A by a
15 broken line. This results in further decreasing the fuel
consumption rate. Note that, when the engine 1 is
quickly accelerated, the engine 1 may perform the
stoichiometric operation in which the engine air-fuel
ratio is made equal to the stoichiometric air-fuel ratio,
20 to thereby ensure the larger output torque.

On the other hand, in this embodiment, the exhaust
gas air-fuel ratio of the exhaust gas flowing into the
catalysts 8a, 10b, and 10a is made lean and rich
alternately and repeatedly, in particular, is made equal
25 to the lean and the rich air-fuel ratios (A/F)_L and
(A/F)_R alternately and repeatedly, as shown in Fig. 43A
by the solid line.

To make the exhaust gas air-fuel ratio of the
exhaust gas flowing into the catalysts 8a, 10b, and 10a
30 lean, the auxiliary engine 120a performs a lean
operation. In particular, to make the exhaust gas
air-fuel ratio of the exhaust gas flowing into the
catalysts 8a, 10b, and 10a equal to the lean air-fuel
ratio (A/F)_L, the exhaust gas air-fuel ratio of the
35 exhaust gas from the auxiliary engine 120a, that is, the
engine air-fuel ratio of the auxiliary engine 120a is
made equal to the lean air-fuel ratio (A/F)_{AL}. In this

embodiment, the exhaust gas air-fuel ratio of the exhaust gas from the engine 1 is made equal to $(A/F)L$, and thus the lean air-fuel ratio $(A/F)AL$ is identical to $(A/F)L$. In other word, in this case, the target air-fuel ratio $(A/F)AT$ of the auxiliary engine 120a is made $(A/F)L$, as shown in Fig. 43A by the two-dot chain line.

To make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a rich, the auxiliary engine 120a performs the rich operation. In particular, to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to a rich air-fuel ratio $(A/F)R$ such as 13.8, the engine air-fuel ratio of the auxiliary engine 120a is made equal to the rich air-fuel ratio $(A/F)AR$, which is smaller or richer than the rich air-fuel ratio $(A/F)R$. In other word, in this case, the target air-fuel ratio $(A/F)AT$ of the auxiliary engine 120a is made $(A/F)AR$, as shown in Fig. 43A by the two-dot chain line. In this way, the auxiliary engine 120a performs the lean and rich operation alternately and repeatedly, while the engine 1 performs the lean operation continuously.

Namely, the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is kept lean when the auxiliary engine 120a performs the lean operation, as shown in Fig. 43B by the solid line, and is changed to rich when the auxiliary engine 120a performs the rich operation, as shown in Fig. 43B by the broken line.

The engine air-fuel ratio of the engine 1 is made equal to the lean air-fuel ratio (A/F) on the basis of the output signals from the air-fuel ratio sensor 29c. The engine air-fuel ratio of the auxiliary engine 120a is controlled to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to the lean and the rich air-fuel ratios $(A/F)L$ and $(A/F)R$ on the basis of the output signals from the

air-fuel ratio sensor 29a.

In this embodiment, the lean operation period, which is a period during which the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalyst 8a, 10b, and 10a is made lean, and the rich operation period, which is a period during which the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is made rich, are controlled in accordance with at least one of the NH_3 amount $S(\text{NH}_3)$ adsorbed in the NH_3 -AO catalyst 10a, and the NO_x amount $S(\text{NO}_x)$ occluded in the NO_x -OR catalyst 10b. Namely, the lean and the rich operation of the auxiliary engine 120a is controlled in accordance with at least one of $S(\text{NH}_3)$ and $S(\text{NO}_x)$. Namely, for example, the engine operation of the auxiliary engine 120a is changed from the lean operation to the rich operation when the adsorbed NH_3 amount exceeds the maximum amount therefor, and is changed from the rich operation to the lean operation when the adsorbed NH_3 amount falls below the minimum amount therefor.

The occluded NO_x amount $S(\text{NO}_x)$ is estimated on the basis of the NO_x amount flowing into the NO_x -OR catalyst 10b, that is, the sum of the NO_x amounts exhausted from the engines 1 and 120a. The adsorbed NH_3 amount $S(\text{NH}_3)$ is estimated on the basis of the synthesized NH_3 amount in the catalyst 8a, which is estimated on the basis of the NO_x amounts exhausted from the engines 1 and 120a, and the released NO_x amount from the NO_x -OR catalyst 10b. Note that the temperatures TTC and TNC representing the temperatures of the catalysts 8a and 10b are detected by the sensor 140, and the temperature TAC representing the temperature of the catalyst 10a is estimated on the basis of the output signals from the sensor 140.

Fig. 44 illustrates the routine for calculating the

fuel injection time TAU for the engine 1.

Referring to Fig. 44, first, in step 180, the basic fuel injection time TB is calculated using the following equation:

$$5 \quad TB = (Q / N) \cdot K$$

In the following step 181, the feedback correction coefficient FAF is calculated, on the basis of the output signals from the sensor 29c. In the following step 182, the lean air-fuel ratio (A/F)L is calculated. In the following step 183, the lean air-fuel ratio (A/F)L is memorized as the target air-fuel ratio (A/F)T. In the following step 184, the fuel injection time TAU is calculated using the following equation:

$$15 \quad TAU = TB \cdot ((A/F)S / (A/F)T) \cdot FAF$$

Each fuel injector 5 injects the fuel for the fuel injection time TAU.

Fig. 45 illustrates the routine for calculating the fuel injection time ATAU for the auxiliary engine 120a.

Referring to Fig. 45, first, in step 190, the basic fuel injection time ATB is calculated using the following equation, on the basis of the engine load AQ/AN and the engine speed AN:

$$ATB = (AQ / AN) \cdot K$$

In the following step 191, the feedback correction coefficient AFAP is calculated on the basis of the output signals from the sensor 29a. The feedback correction coefficient AFAP is for controlling the engine air-fuel ratio of the auxiliary engine 120a to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to the lean or the rich air-fuel ratio (A/F)L, (A/F)R. In the following step 192, it is judged whether FRICH, which is controlled in the routine shown in Fig. 10, is made 1. If FRICH = 1, that is, if the rich operation is to be performed, the routine goes to step 193, where the rich air-fuel ratio (A/F)AR is calculated. In the following step 194, the rich air-fuel ratio (A/F)AR is memorized as

the target air-fuel ratio (A/F)AT. Next, the routine goes to step 197.

Contrarily, if FRICH is zero in step 192, that is, if the lean operation is to be performed, the routine
5 goes to step 195, where the lean air-fuel ratio (A/F)AL is calculated. In the following step 196, the lean air-fuel ratio (A/F)AL is memorized as the target air-fuel ratio (A/F)AT. Next, the routine goes to step 197.

10 In step 197, the fuel injection time ATAU is calculated using the following equation:

$$ATAU = ATB \cdot ((A/F)S / (A/F)AT) \cdot AFAF$$

The fuel injector 125 injects the fuel for the fuel injection time ATAU.

15 In the embodiment shown in Fig. 42, the engine 1 performs the lean operation continuously and the auxiliary engine 120a performs the lean and the rich operation alternately and repeatedly. In this case, the crank shafts thereof are different to each other, and
20 thus the drivability is prevented from being deteriorated, while ensuring the good purification of the exhaust gas. Further, the auxiliary engine 120a provides an additional output torque. Furthermore, if the engine 1 is originally provided with the auxiliary
25 engine 120a, there is no need to newly provide the making-rich device 120, and thereby the structure of the exhaust gas purifying device is made simpler. The other constructions of the exhaust purifying device and the operation thereof are the same as those in the engine
30 shown in Fig. 1, and thus the explanations therefor are omitted.

Fig. 46 illustrates still further another embodiment. In Fig. 46, constituent elements the same as those in Figs. 1 and 42 are given the same reference
35 numerals.

In this embodiment, the making-rich device 120 comprises a burner 120b, of which an air-fuel ratio is

controllable. The exhaust gas of the burner 120b flows into the TW catalyst 8a via the pipes 127 and 129, and is mixed with the exhaust gas from the engine 1.

5 Next, the exhaust gas purifying method in this embodiment will be explained with respect to Fig. 47. The exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is made the lean and the rich air-fuel ratios $(A/F)_L$ and $(A/F)_R$, alternately and repeatedly, as in the preceding embodiments.

10 However, in this embodiment, the burner 120b is stopped and the engine 1 performs the lean operation with the lean air-fuel ratio $(A/F)_L$, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to $(A/F)_L$. The

15 burner 120b performs the rich operation with the rich air-fuel ratio $(A/F)_R$ and the engine 1 performs the lean operation with the lean air-fuel ratio $(A/F)_L$, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to

20 $(A/F)_R$. Accordingly, the burner 120b is operated and stopped alternately and repeatedly.

 Fuel for the burner 120b may be hydrocarbon such as gasoline, isooctane, hexane, heptane, gas oil, and kerosene or a hydrocarbon which can be stored in a liquid

25 state, such as butane or propane. However, if fuel same as that for the engine 1 is used for the burner 120b, there is no need for providing an additional fuel tank, and thus gasoline is used in this embodiment.

 While the burner 120b is connected to the catalytic

30 converter 9 via the pipes 127 and 129, in this embodiment, it may be provided integrally with the converter 9 or the catalyst 8a. Further, the burner 120b may be continuously operated and perform the lean operation with the lean air-fuel ratio such as $(A/F)_L$

35 when making the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a lean. The other constructions of the exhaust purifying device

and the operation thereof are the same as those in the engine shown in Fig. 42, and thus the explanations therefor are omitted.

Fig. 48 illustrates still further another embodiment. In Fig. 48, constituent elements the same as those in Figs. 1 and 42 are given the same reference numerals.

In this embodiment, the engine 1 is constructed as a diesel engine, while the spark-ignition type engine may be adopted. Referring to Fig. 48, each fuel injector 5 injects fuel into the corresponding combustion chamber of the cylinder directly. Also, an air-flow meter 27a is arranged in the intake duct 4. The air-flow meter 27a generates an output voltage proportional to the intake air amount, and the output voltage thereof is input via an AD converter 28a to the input port 25.

As shown in Fig. 48, the making-rich device 120 comprises a reducing agent injector 120c arranged in the outlet of the exhaust manifold 7 for adding a reducing agent into the exhaust gas. The reducing agent may be hydrocarbon such as gasoline, isooctane, hexane, heptane, gas oil, and kerosene or a hydrocarbon which can be stored in a liquid state, such as butane or propane, but is preferable to be the same as that for the engine 1.

The engine 1 performs the lean operation continuously. If a diesel engine performs the rich operation, the engine exhausts a large amount of the black smoke. The black smoke includes a large amount of unburned HC, and the TW catalyst 8a cannot purify the HC sufficiently. On the other hand, providing an additional catalyst only for purifying such HC is undesired. Therefore, the diesel engine shown in Fig. 48 performs the lean operation continuously.

Next, the exhaust gas purifying method in this embodiment will be explained with respect to Fig. 49. The exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is made the lean and

the rich air-fuel ratios $(A/F)_L$ and $(A/F)_R$, alternately and repeatedly. To this end, the reducing agent injection by the reducing agent injector 120b is stopped and the engine 1 performs the lean operation with the lean air-fuel ratio $(A/F)_L$, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to $(A/F)_L$. The reducing agent injector 120c injects the reducing agent and the engine 1 performs the lean operation with the lean air-fuel ratio $(A/F)_L$, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to $(A/F)_R$. That is, the reducing agent injector 120c injects the reducing agent by an amount required to make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10a, and 10b equal to $(A/F)_R$. In this way, the reducing agent injection by the injector 120c is operated and stopped alternately and repeatedly.

Note that, in the above-mentioned embodiment, when the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a is to be made equal to $(A/F)_L$, the reducing agent injection is stopped while the engine 1 performs the lean operation with the lean air-fuel ratio $(A/F)_L$. Alternatively, the reducing agent injector 120c may inject a very small amount of the reducing agent and the engine 1 may perform the lean operation with the lean air-fuel ratio leaner than $(A/F)_L$, to thereby make the exhaust gas air-fuel ratio of the exhaust gas flowing into the catalysts 8a, 10b, and 10a equal to $(A/F)_L$.

Also, a burner may be arranged in the exhaust passage upstream of the TW catalyst 8a to consume the oxygen existing in the exhaust gas, to thereby make the exhaust gas air-fuel ratio rich.

According to the present invention, it is possible to provide a method and a device for purifying an exhaust gas of an engine which can purify the exhaust gas

WO 97/17532

PCT/JP96/03205

- 69 -

sufficiently with a simple structure.

While the invention has been described by reference to specific embodiments chosen for purposes of illustration, it should be apparent that numerous
5 modifications could be made thereto by those skilled in the art without departing from the basic concept and scope of the invention.

WO 97/17532

PCT/JP96/03205

- 70 -

CLAIMS

1. A method for purifying an exhaust gas of an engine, comprising, in turn:

5 forming an exhaust gas portion of which an exhaust gas air-fuel ratio is lean, and an exhaust gas portion of which the exhaust gas air-fuel ratio is rich, from the exhaust gas of the engine, alternately and repeatedly; and

10 contacting the exhaust gas portions an NH_3 synthesizing catalyst and an exhaust gas purifying catalyst comprised of at least one selected from the group consisted of an NH_3 adsorbing and oxidizing ($\text{NH}_3\text{-AO}$) catalyst and a NO_x occluding and reducing ($\text{NO}_x\text{-OR}$) catalyst, in turn, the NH_3 synthesizing catalyst
15 synthesizing NH_3 from at least a part of NO_x in the inflowing exhaust gas when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, and passing NO_x in the inflowing exhaust gas therethrough when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean,
20 the $\text{NH}_3\text{-AO}$ catalyst adsorbing NH_3 in the inflowing exhaust gas therein, and desorbing the adsorbed NH_3 therefrom and oxidizing the NH_3 when an NH_3 concentration in the inflowing exhaust gas becomes lower, and the $\text{NO}_x\text{-OR}$ catalyst occluding NO_x in the inflowing exhaust
25 gas therein when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, and releasing the occluded NO_x therefrom and reducing the NO_x when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich.

30 2. A method according to claim 1, further comprising controlling an engine air-fuel ratio of the engine to make the engine air-fuel ratio lean to thereby form the exhaust gas portion of which the exhaust gas air-fuel ratio is lean, and to make the engine air-fuel ratio rich to thereby form the exhaust gas portion of
35 which the exhaust gas air-fuel ratio is rich.

3. A method according to claim 2, wherein the engine air-fuel ratio of the engine is made lean for a lean period, and the engine air-fuel ratio of the engine is made rich for a rich period, and wherein the lean and the rich periods are set in accordance with the engine operating condition, respectively.

4. A method according to claim 3, wherein the engine is provided with a plurality of cylinders or cylinder groups of which the exhaust stroke periods are different to each other, and wherein the lean period is set as the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean, and the rich period is set as the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich.

5. A method according to claim 4, wherein the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean and the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich is set to vary the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich in every cycle, the cycle being formed by one lean period and one rich period which are successive.

6. A method according to claim 4, wherein the lean and the rich period are controlled in accordance with a number ratio which is a ratio of the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean to the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich, the number ratio being set in accordance with the engine operating condition.

7. A method according to claim 6, wherein the number ratio is equal to or larger than the total number of the cylinders or cylinder groups of the engine.

8. A method according to claim 6, wherein the number ratio becomes larger as the engine load becomes

WO 97/17532

PCT/JP96/03205

- 72 -

higher when the engine load is low, and becomes smaller as the engine load become higher when the engine load is high.

5 9. A method according to claim 6, wherein the number ratio becomes larger as the intake air amount becomes larger when the intake air amount is small, and becomes smaller as the intake air amount become larger when the intake air amount is large.

10 10. A method according to claim 2, the engine being an internal combustion engine of spark ignition type, and the method further comprising controlling the ignition timing of the engine in accordance with the engine air-fuel ratio of the engine.

15 11. A method according to claim 1, wherein a making-rich device, different from the engine, is arranged in the exhaust passage of an engine upstream of the NH_3 synthesizing catalyst for making the exhaust gas air-fuel ratio of the exhaust gas of the engine rich, and wherein the method further comprises keeping an engine
20 air-fuel ratio of the engine lean, and stopping a making-rich operation of the making-rich device to thereby form the exhaust gas of which the exhaust gas air-fuel ratio is lean, and performing the making-rich operation of the making-rich device to thereby form the
25 exhaust gas of which the exhaust gas air-fuel ratio is rich.

30 12. A method according to claim 11, wherein the making-rich device is provided with: a combustor of which an air-fuel ratio is controllable; and an introducing passage for introducing the exhaust gas of the combustor into the exhaust passage upstream of the NH_3 synthesizing catalyst, and wherein the making-rich operation of the making-rich device is performed by making an air-fuel ratio of the combustor rich and adding
35 the exhaust gas of the combustor to the exhaust gas of the engine.

13. A method according to claim 12, wherein the combustor is an auxiliary internal combustion engine having a crank shaft different from that of the engine.

14. A method according to claim 12, wherein the combustor is a burner.

15. A method according to claim 11, wherein the making-rich device is provided with a reducing agent injector for feeding a reducing agent into the exhaust passage upstream of the NH_3 synthesizing catalyst, the making-rich operation of the reducing agent injector being performed by adding the reducing agent to the exhaust gas of the engine.

16. A method according to claim 15, wherein the reducing agent is a hydrocarbon such as gasoline, isooctane, hexane, heptane, gas oil, and kerosene or a hydrocarbon which can be stored in a liquid state, such as butane or propane.

17. A method according to claim 1, wherein the exhaust gas purifying catalyst is comprised of at least the NH_3 -AO catalyst, wherein the method further comprises estimating an amount of NH_3 adsorbed in the NH_3 -AO catalyst, and wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich or from rich to lean in accordance with the estimated adsorbed NH_3 amount.

18. A method according to claim 17, wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from rich to lean when the estimated adsorbed NH_3 amount exceeds over a predetermined upper threshold.

19. A method according to claim 17, wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich when the estimated adsorbed NH_3 amount falls below a predetermined lower threshold.

20. A method according to claim 17, wherein the adsorbed NH_3 amount is estimated on the basis of an NH_3 amount flowing into the NH_3 -AO catalyst when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH_3 -AO catalyst is rich, and on the basis of the desorbed NH_3 amount when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH_3 -AO catalyst is lean.

21. A method according to claim 20, wherein the NH_3 amount flowing into the NH_3 -AO catalyst is estimated on the basis of a NO_x amount flowing into the NH_3 synthesizing catalyst and an NH_3 synthesizing efficiency of the NH_3 synthesizing catalyst.

22. A method according to claim 1, wherein the exhaust gas purifying catalyst is comprised of at least the NO_x -OR catalyst, wherein the method further comprises estimating an amount of NO_x occluded in the NO_x -OR catalyst, and wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich or from rich to lean in accordance with the estimated occluded NO_x amount.

23. A method according to claim 22, wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich when the estimated occluded NO_x amount exceeds over a predetermined upper threshold.

24. A method according to claim 22, wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from rich to lean when the estimated occluded NO_x amount falls below a predetermined lower threshold.

25. A method according to claim 22, wherein the occluded NO_x amount is estimated on the basis of a NO_x amount flowing into the NO_x -OR catalyst when the exhaust gas air-fuel ratio of the exhaust gas flowing into the

NO_x-OR catalyst is lean, and on the basis of the released NO_x amount when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NO_x-OR catalyst is rich.

26. A method according to claim 1, wherein the
5 exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich or from rich to lean in accordance with the engine operating condition.

27. A method according to claim 1, wherein the
10 exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich or from rich to lean gradually with a changing rate.

28. A method according to claim 27, wherein the
15 changing rate when the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from lean to rich is larger than that when the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is changed from rich to lean.

29. A method according to claim 27, wherein the
20 changing rate is set in accordance with the engine operating condition.

30. A method according to claim 29, wherein the
25 changing rate becomes smaller as the engine load becomes higher.

31. A method according to claim 1, wherein the
exhaust gas air-fuel ratio of the exhaust gas portion is set in accordance with the engine operating condition.

32. A method according to claim 31, wherein the
30 exhaust gas air-fuel ratio of the exhaust gas portion of which the exhaust gas air-fuel ratio is lean becomes larger as the engine load becomes higher when the engine load is low, and becomes smaller as the engine load becomes higher when the engine load is high.

33. A method according to claim 31, wherein the
35 exhaust gas air-fuel ratio of the exhaust gas portion of

which the exhaust gas air-fuel ratio is rich becomes smaller when the intake air amount of the engine becomes larger.

5 34. A method according to claim 1, wherein the exhaust gas air-fuel ratio of one of the exhaust gas portions is set in accordance with the exhaust gas air-fuel ratio of the other.

10 35. A method according to claim 1, wherein a period during which the exhaust gas portion of which the exhaust gas air-fuel ratio is lean is formed, is longer than that during which the exhaust gas portion of which the exhaust gas air-fuel ratio is rich is formed.

15 36. A method according to claim 1, wherein the exhaust gas air-fuel ratio of the exhaust gas portion to be contacted with the catalysts is made equal to a target air-fuel ratio on the basis of output signals of an air-fuel ratio sensor arranged in an exhaust passage of the engine adjacent to an inlet of the NH_3 synthesizing catalyst.

20 37. A method according to claim 1, the engine further having a muffler arranged in an exhaust passage thereof, wherein the exhaust gas purifying catalyst is comprised of at least the NH_3 -AO catalyst, and wherein the NH_3 -AO catalyst is housed in the muffler.

25 38. A method according to claim 1, wherein the exhaust gas purifying catalyst is comprised of at least the NO_x -OR catalyst, and wherein the NH_3 synthesizing catalyst and the NO_x -OR catalyst are carried on a common substrate.

30 39. A method according to claim 1, wherein the exhaust gas purifying catalyst is comprised of both of the NH_3 -AO catalyst and the NO_x -OR catalyst, and wherein the NH_3 -AO catalyst and the NO_x -OR catalyst are arranged in an exhaust passage of the engine, in series.

35 40. A method according to claim 39, wherein the NH_3 -AO catalyst is arranged in the exhaust passage

downstream of the NO_x-OR catalyst.

41. A method according to claim 1, wherein the exhaust gas purifying catalyst is comprised of both of the NH₃-AO catalyst and the NO_x-OR catalyst, and wherein
5 the NH₃-AO catalyst and the NO_x-OR catalyst are laminated to each other on a common substrate.

42. A method according to claim 1, wherein the NH₃ synthesizing catalyst is a three-way catalyst including at least one precious metal such as palladium, platinum,
10 and rhodium.

43. A method according to claim 1, wherein the NO_x-OR catalyst includes: at least one substance selected from alkali metals such as potassium, sodium, lithium, and cesium, alkali earth metals such as barium
15 and calcium, rare earth metals such as lanthanum and yttrium, and transition metals such as iron and copper; and precious metals such as palladium, platinum, and rhodium.

44. A method according to claim 1, further
20 comprising contacting the exhaust gas portions an NH₃ purifying catalyst for purifying NH₃ in the inflowing exhaust gas, after contacting the exhaust gas portions the exhaust gas purifying catalyst.

45. A method according to claim 44, wherein the NH₃
25 purifying catalyst includes at least one substance selected from precious metals such as palladium, platinum, and rhodium, and transition metals such as iron and copper.

46. A method according to claim 44, the NH₃
30 purifying catalyst purifying NH₃ under the oxidizing atmosphere, wherein the method further comprises keeping the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH₃ purifying catalyst lean.

47. A device for purifying an exhaust gas of an
35 engine having an exhaust passage, comprising:

WO 97/17532

PCT/JP96/03205

- 78 -

exhaust gas portion forming means arranged in the engine or the exhaust passage for forming an exhaust gas portion of which an exhaust gas air-fuel ratio is lean, and an exhaust gas portion of which the exhaust gas air-fuel ratio is rich, from the exhaust gas of the engine, alternately and repeatedly;

an NH_3 synthesizing catalyst arranged in the exhaust passage downstream of the exhaust gas portion forming means, the NH_3 synthesizing catalyst synthesizing NH_3 from at least a part of NO_x in the inflowing exhaust gas when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich, and passing NO_x in the inflowing exhaust gas therethrough when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean; and

an exhaust gas purifying catalyst arranged in the exhaust passage downstream of the NH_3 synthesizing catalyst, the exhaust gas purifying catalyst comprising at least one selected from the group consisting of an NH_3 adsorbing and oxidizing ($\text{NH}_3\text{-AO}$) catalyst and a NO_x occluding and reducing ($\text{NO}_x\text{-OR}$) catalyst, the $\text{NH}_3\text{-AO}$ catalyst adsorbing NH_3 in the inflowing exhaust gas therein, and desorbing the adsorbed NH_3 therefrom and oxidizing the NH_3 when the NH_3 concentration in the inflowing exhaust gas becomes lower, and the $\text{NO}_x\text{-OR}$ catalyst occluding NO_x in the inflowing exhaust gas therein when the exhaust gas air-fuel ratio of the inflowing exhaust gas is lean, and releasing the occluded NO_x therefrom and reducing the NO_x when the exhaust gas air-fuel ratio of the inflowing exhaust gas is rich.

48. A device according to claim 47, wherein the exhaust gas portion forming means comprises an engine air-fuel ratio control means for controlling an engine air-fuel ratio of the engine to make the engine air-fuel ratio lean to thereby form the exhaust gas portion of which the exhaust gas air-fuel ratio is lean, and to make

the engine air-fuel ratio rich to thereby form the exhaust gas portion of which the exhaust gas air-fuel ratio is rich.

49. A device according to claim 48, wherein the engine air-fuel ratio control means makes the engine air-fuel ratio lean for a lean period, and makes the engine air-fuel ratio rich for a rich period, and wherein the lean and the rich periods are set in accordance with the engine operating condition, respectively.

50. A device according to claim 49, wherein the engine is provided with a plurality of cylinders or cylinder groups of which the exhaust stroke periods are different to each other, and wherein the lean period is set as the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean, and the rich period is set as the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich.

51. A device according to claim 50, wherein the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean and the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich are set to vary the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich in every cycle, the cycle being formed by one lean period and one rich period which are successive.

52. A device according to claim 50, wherein the lean and the rich period are controlled in accordance with a number ratio which is a ratio of the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made lean to the number of the cylinders or cylinder groups of which the engine air-fuel ratio is to be made rich, the number ratio being set in accordance with the engine operating condition.

53. A device according to claim 52, wherein the number ratio is equal to or larger than the total number

WO 97/17532

PCT/JP96/03205

- 80 -

of the cylinders or cylinder groups of the engine.

54. A device according to claim 52, wherein the number ratio becomes larger as the engine load becomes higher when the engine load is low, and becomes smaller as the engine load become higher when the engine load is high.

55. A device according to claim 52, wherein the number ratio becomes larger as the intake air amount becomes larger when the intake air amount is small, and becomes smaller as the intake air amount become larger when the intake air amount is large.

56. A device according to claim 48, the engine being an internal combustion engine of spark ignition type, and the device further comprising ignition timing control means for controlling the ignition timing of the engine in accordance with the engine air-fuel ratio of the engine.

57. A device according to claim 47, wherein the exhaust gas portion forming means comprises making-rich means, different from the engine, arranged in the exhaust passage upstream of the NH_3 synthesizing catalyst for making the exhaust gas air-fuel ratio of the exhaust gas of the engine rich, and keeping means for keeping the engine air-fuel ratio of the engine lean, and wherein the making-rich means stops a making-rich operation thereof to thereby form the exhaust gas of which the exhaust gas air-fuel ratio is lean, and performs the making-rich operation thereof to thereby form the exhaust gas of which the exhaust gas air-fuel ratio is rich.

58. A device according to claim 57, wherein the making-rich means comprises: a combustor of which an air-fuel ratio is controllable; and an introducing passage for introducing the exhaust gas of the combustor into the exhaust passage upstream of the NH_3 synthesizing catalyst, and wherein the making-rich means performs the making-rich operation thereof by making an air-fuel ratio

of the combustor rich and adding the exhaust gas of the combustor to the exhaust gas of the engine.

59. A device according to claim 58, wherein the combustor is an auxiliary internal combustion engine having a crank shaft different from that of the engine.

60. A device according to claim 58, wherein the combustor is a burner.

61. A device according to claim 57, wherein the making-rich means comprises a reducing agent injector for feeding a reducing agent into the exhaust passage upstream of the NH_3 synthesizing catalyst, the reducing agent injector performing the making-rich operation thereof by adding the reducing agent to the exhaust gas of the engine.

62. A device according to claim 61, wherein the reducing agent is a hydrocarbon such as gasoline, isooctane, hexane, heptane, gas oil, and kerosene or a hydrocarbon which can be stored in a liquid state, such as butane or propane.

63. A device according to claim 47, wherein the exhaust gas purifying catalyst comprises at least the NH_3 -AO catalyst, wherein the device further comprises adsorbed NH_3 amount estimating means for estimating an amount of NH_3 adsorbed in the NH_3 -AO catalyst, and wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich or from rich to lean in accordance with the estimated adsorbed NH_3 amount.

64. A device according to claim 63, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from rich to lean when the estimated adsorbed NH_3 amount exceeds a predetermined upper threshold.

65. A device according to claim 63, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby

from lean to rich when the estimated adsorbed NH_3 amount falls below a predetermined lower threshold.

66. A device according to claim 63, wherein the adsorbed NH_3 amount estimating means estimates the
5 adsorbed NH_3 amount on the basis of an NH_3 amount flowing into the NH_3 -AO catalyst when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH_3 -AO catalyst is rich, and on the basis of the desorbed NH_3 amount when
10 the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH_3 -AO catalyst is lean.

67. A device according to claim 66, wherein the adsorbed NH_3 amount estimating means estimates the NH_3 amount flowing into the NH_3 -AO catalyst on the basis of a
15 NO_x amount flowing into the NH_3 synthesizing catalyst and an NH_3 synthesizing efficiency of the NH_3 synthesizing catalyst.

68. A device according to claim 47, wherein the exhaust gas purifying catalyst comprises at least the NO_x -OR catalyst, wherein the device further comprises
20 occluded NO_x amount estimating means for estimating an amount of NO_x occluded in the NO_x -OR catalyst, and wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich or from rich to lean in
25 accordance with the estimated occluded NO_x amount.

69. A device according to claim 68, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich when the estimated occluded NO_x amount
30 exceeds a predetermined upper threshold.

70. A device according to claim 68, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from rich to lean when the estimated occluded NO_x amount
35 falls below a predetermined lower threshold.

71. A device according to claim 68, wherein the occluded NO_x amount estimating means estimates the occluded NO_x amount on the basis of a NO_x amount flowing into the NO_x -OR catalyst when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NO_x -OR catalyst is lean, and on the basis of the released NO_x amount when the exhaust gas air-fuel ratio of the exhaust gas flowing into the NO_x -OR catalyst is rich.

72. A device according to claim 47, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich or from rich to lean in accordance with the engine operating condition.

73. A device according to claim 47, wherein the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich or from rich to lean gradually with a changing rate.

74. A device according to claim 73, wherein the changing rate when the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from lean to rich is larger than that when the exhaust gas portion forming means changes the exhaust gas air-fuel ratio of the exhaust gas portion formed thereby from rich to lean.

75. A device according to claim 73, wherein the changing rate is set in accordance with the engine operating condition.

76. A device according to claim 75, wherein the changing rate becomes smaller as the engine load becomes higher.

77. A device according to claim 47, wherein the exhaust gas air-fuel ratio of the exhaust gas portion is set in accordance with the engine operating condition.

78. A device according to claim 77, wherein the exhaust gas air-fuel ratio of the exhaust gas portion of

which the exhaust gas air-fuel ratio is lean becomes larger as the engine load becomes higher when the engine load is low, and becomes smaller as the engine load becomes higher when the engine load is high.

5 79. A device according to claim 77, wherein the exhaust gas air-fuel ratio of the exhaust gas portion of which the exhaust gas air-fuel ratio is rich becomes smaller when the intake air amount of the engine becomes larger.

10 80. A device according to claim 47, wherein the exhaust gas air-fuel ratio of one of the exhaust gas portions is set in accordance with the exhaust gas air-fuel ratio of the other.

15 81. A device according to claim 47, wherein a period during which the exhaust gas portion forming means forms the exhaust gas portion of which the exhaust gas air-fuel ratio is lean is longer than that during which the exhaust gas portion forming means forms the exhaust gas portion of which the exhaust gas air-fuel ratio is rich.

20 82. A device according to claim 47, further comprising an air-fuel ratio sensor arranged in the exhaust passage between the exhaust gas portion forming means and the NH_3 synthesizing catalyst, and wherein the exhaust gas portion forming means makes the exhaust gas air-fuel ratio the exhaust gas portions formed thereby equal to a target air-fuel ratio on the basis of the output signals of the air-fuel ratio sensor.

25 83. A device according to claim 47, the engine further having a muffler arranged in the exhaust passage, wherein the exhaust gas purifying catalyst comprises at least the NH_3 -AO catalyst, and wherein the NH_3 -AO catalyst is housed in the muffler.

30 84. A device according to claim 47, wherein the exhaust gas purifying catalyst comprises at least the NO_x -OR catalyst, and wherein the NH_3 synthesizing

catalyst and the NO_x-OR catalyst are carried on a common substrate.

85. A device according to claim 47, wherein the exhaust gas purifying catalyst comprises both of the
5 NH₃-AO catalyst and the NO_x-OR catalyst, and wherein the NH₃-AO catalyst and the NO_x-OR catalyst are arranged in the exhaust passage in series.

86. A device according to claim 85, wherein the NH₃-AO catalyst is arranged in the exhaust passage
10 downstream of the NO_x-OR catalyst.

87. A device according to claim 47, wherein the exhaust gas purifying catalyst comprises both of the NH₃-AO catalyst and the NO_x-OR catalyst, and wherein the NH₃-AO catalyst and the NO_x-OR catalyst are laminated to
15 each other on a common substrate.

88. A device according to claim 47, wherein the NH₃ synthesizing catalyst is a three-way catalyst including at least one precious metal such as palladium, platinum, and rhodium.

89. A device according to claim 47, wherein the NO_xOR catalyst includes: at least one substance selected from alkali metals such as potassium, sodium, lithium, and cesium, alkali earth metals such as barium and calcium, rare earth metals such as lanthanum and yttrium,
20 and transition metals such as iron and copper; and precious metals such as palladium, platinum, and rhodium.

90. A device according to claim 47, further comprising an NH₃ purifying catalyst arranged downstream of the exhaust gas purifying catalyst for purifying NH₃,
30 in the inflowing exhaust gas.

91. A device according to claim 90, wherein the NH₃ purifying catalyst includes at least one substance selected from precious metals such as palladium, platinum, and rhodium, and transition metals such as iron
35 and copper.

WO 97/17532

PCT/JP96/03205

- 86 -

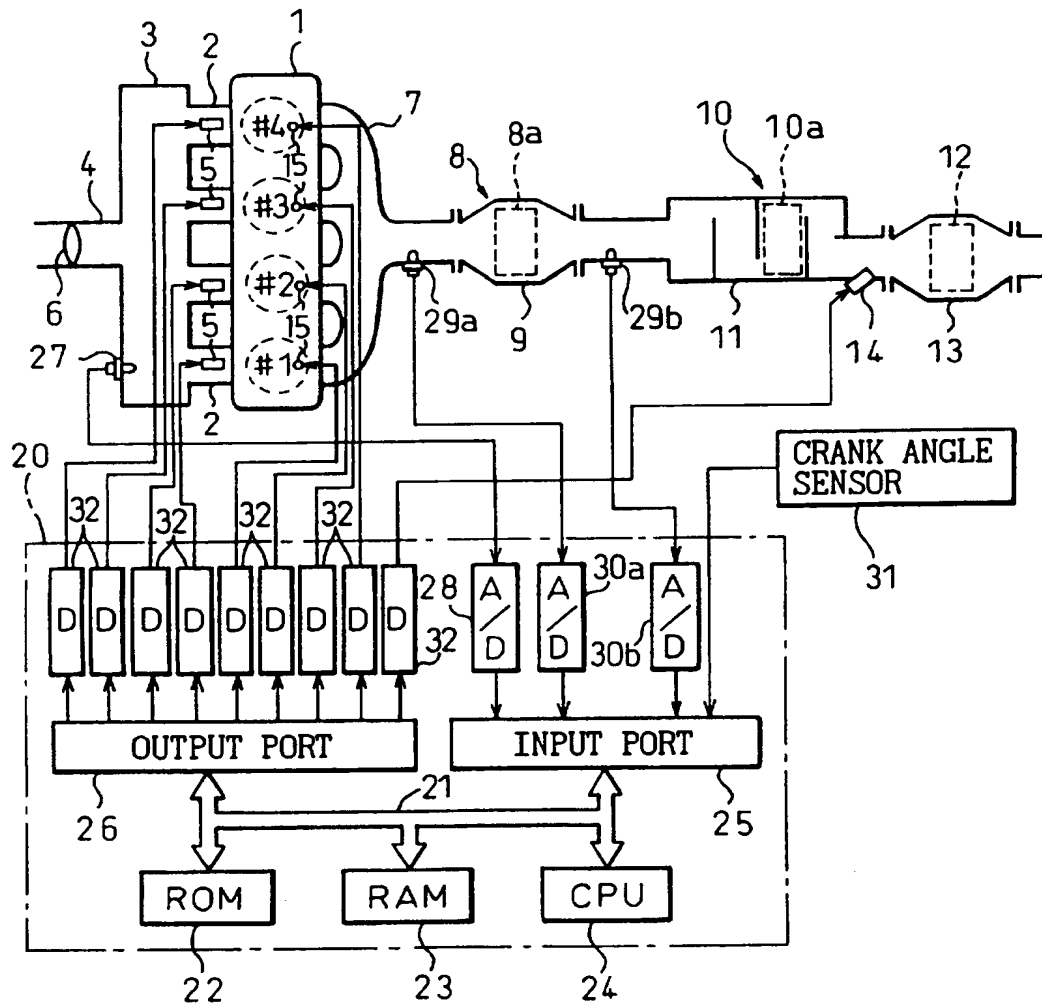
92. A device according to claim 90, the NH₃ purifying catalyst purifying NH₃ under the oxidizing atmosphere, wherein the device further comprises keeping-lean means arranged in the exhaust passage between the exhaust gas purifying catalyst and the NH₃ purifying catalyst for keeping the exhaust gas air-fuel ratio of the exhaust gas flowing into the NH₃ purifying catalyst lean.

WO 97/17532

PCT/JP96/03205

1/44

Fig. 1



WO 97/17532

PCT/JP96/03205

2/44

Fig.2A

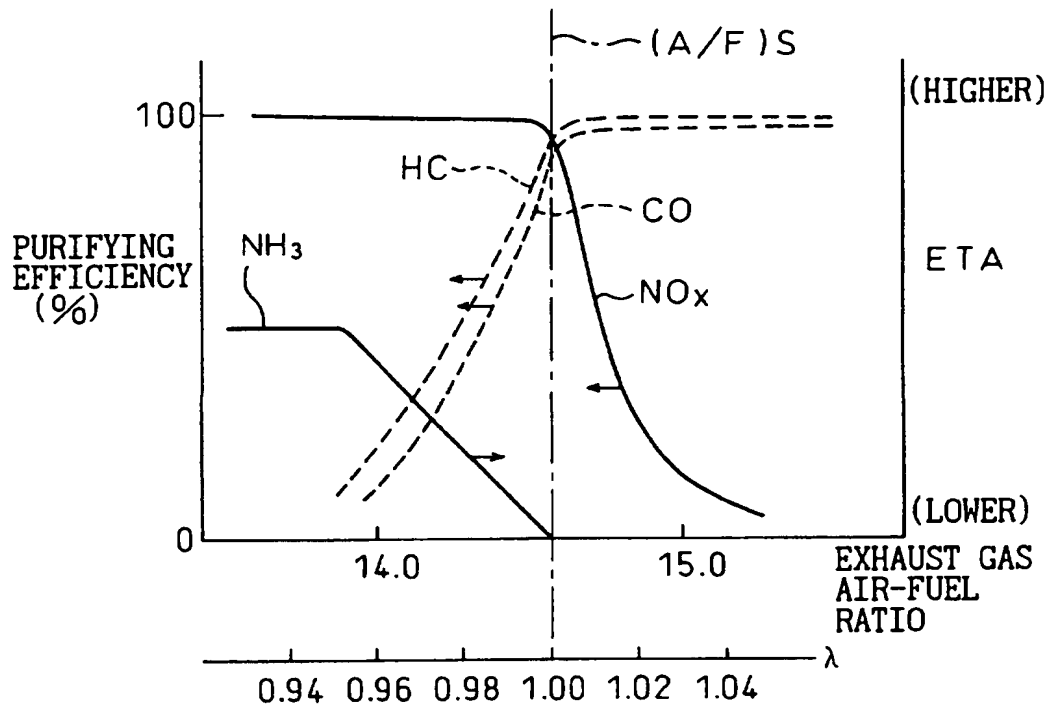
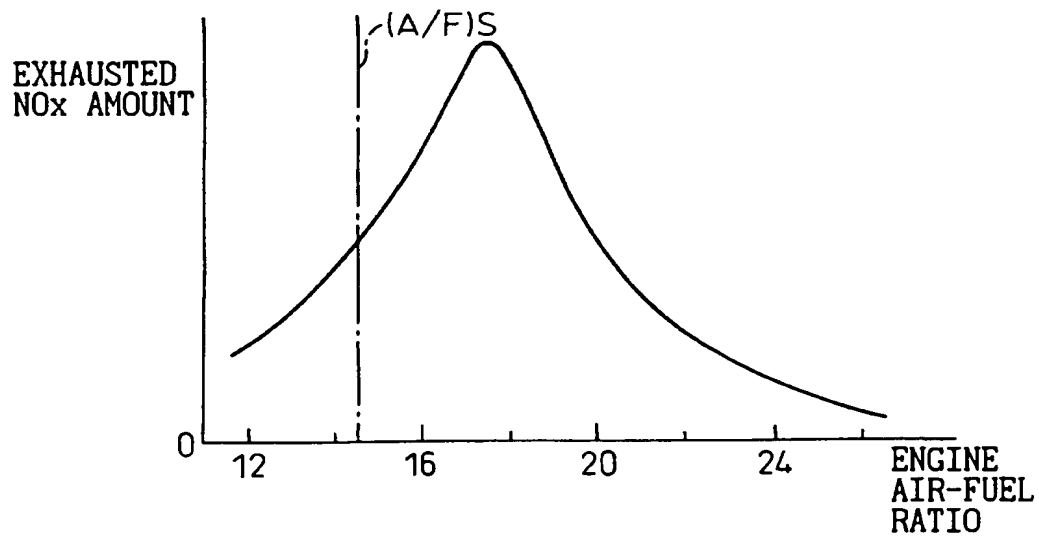


Fig.2B

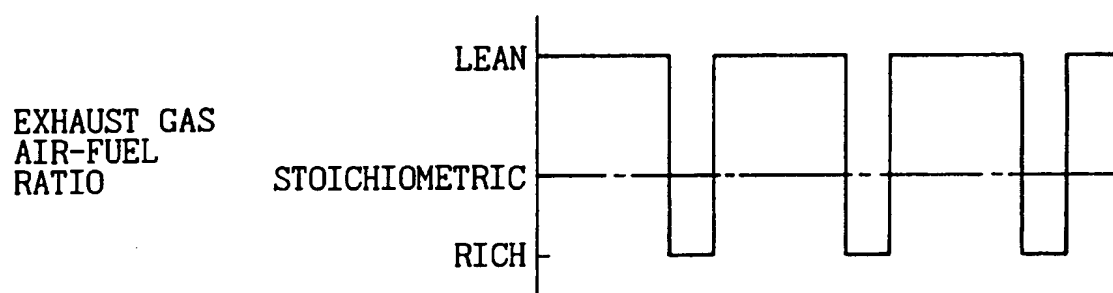


WO 97/17532

PCT/JP96/03205

3/
44

Fig. 3



4/44

Fig. 4A

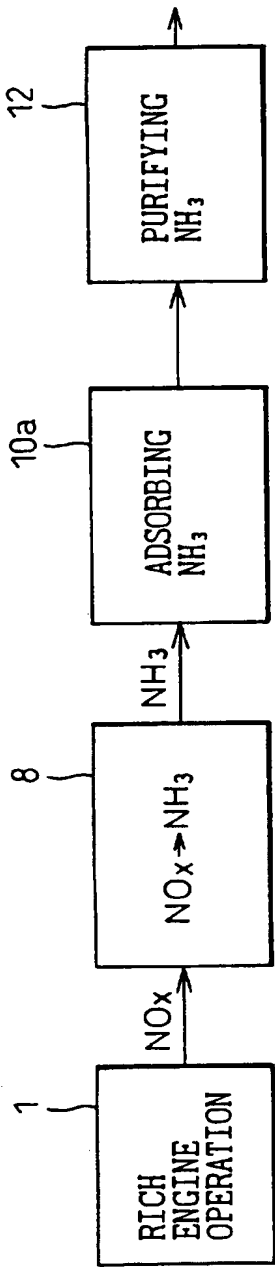
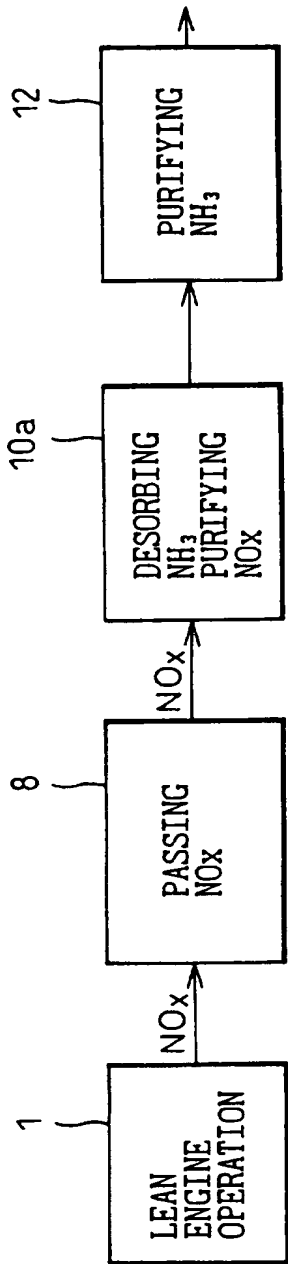


Fig. 4B

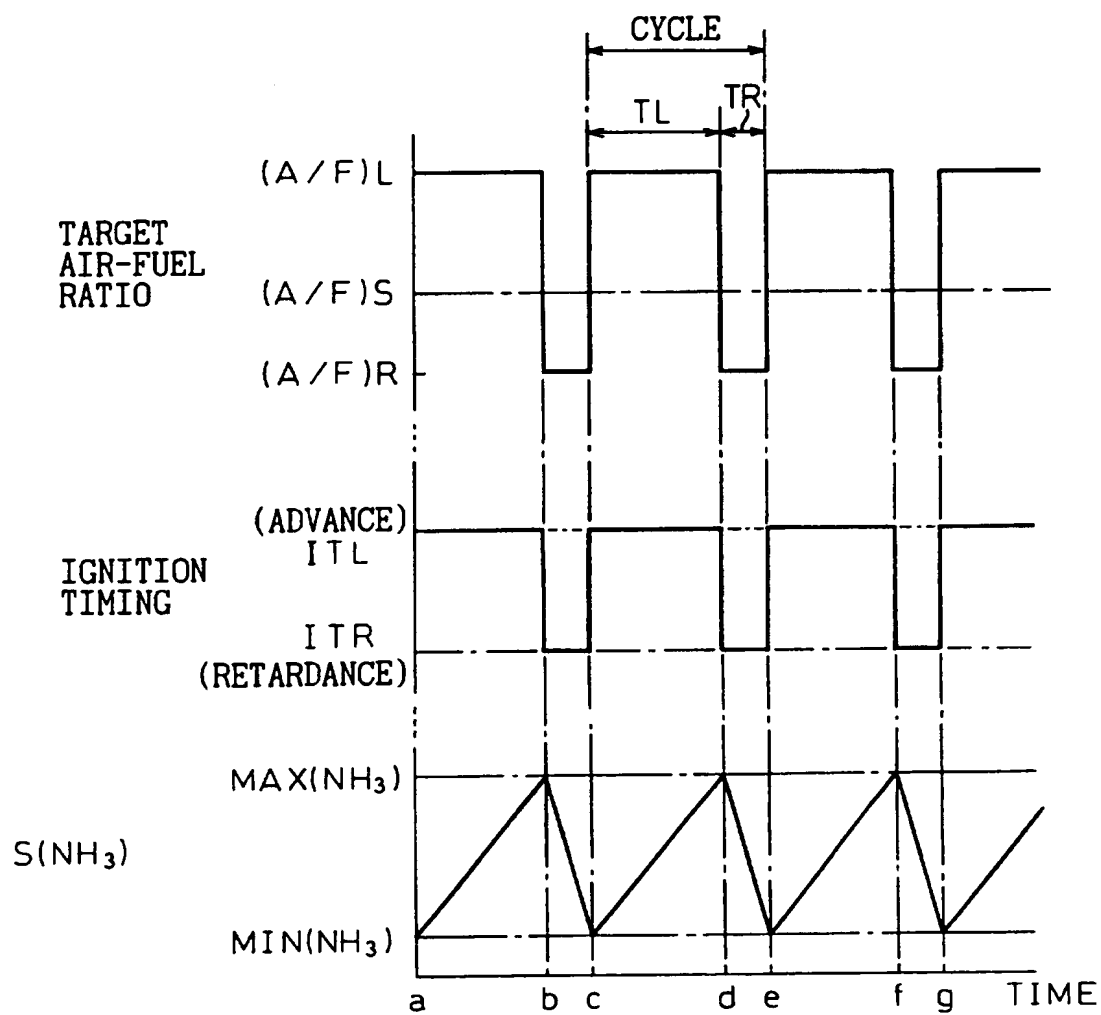


WO 97/17532

PCT/JP96/03205

5/44

Fig.5



WO 97/17532

PCT/JP96/03205

6/
44

Fig.6A

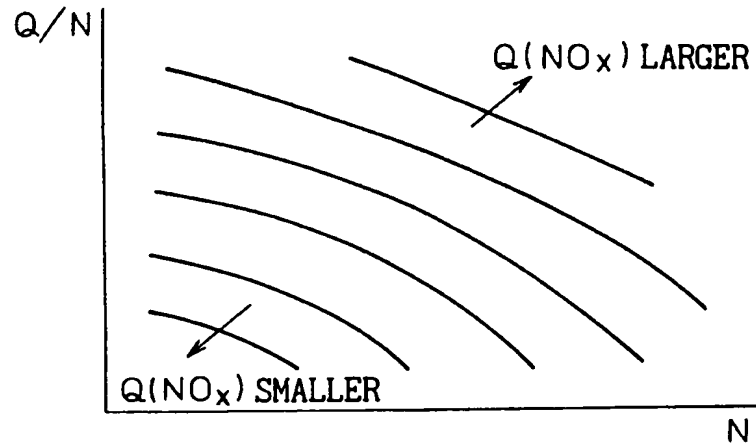
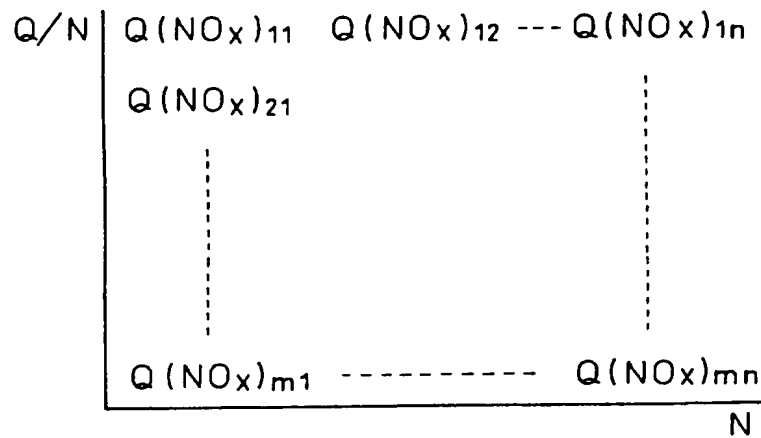


Fig.6B

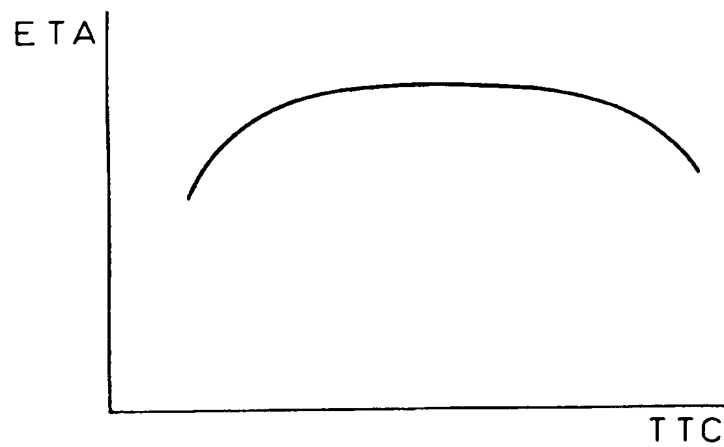


WO 97/17532

PCT/JP96/03205

7/
44

Fig.7



WO 97/17532

PCT/JP96/03205

8/44

Fig.8A

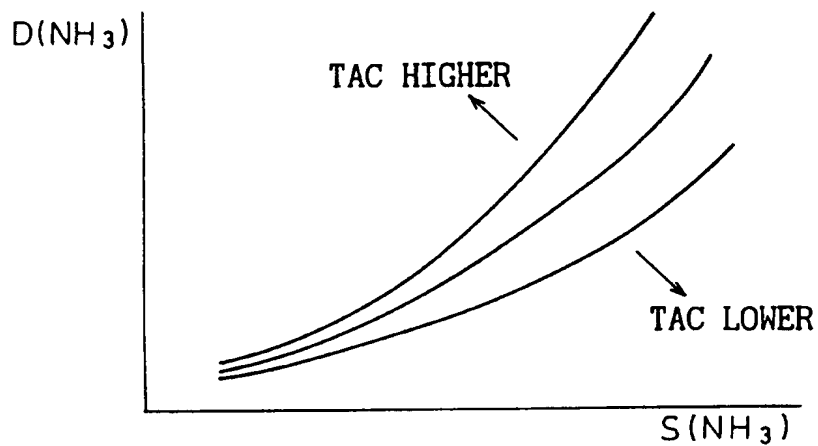
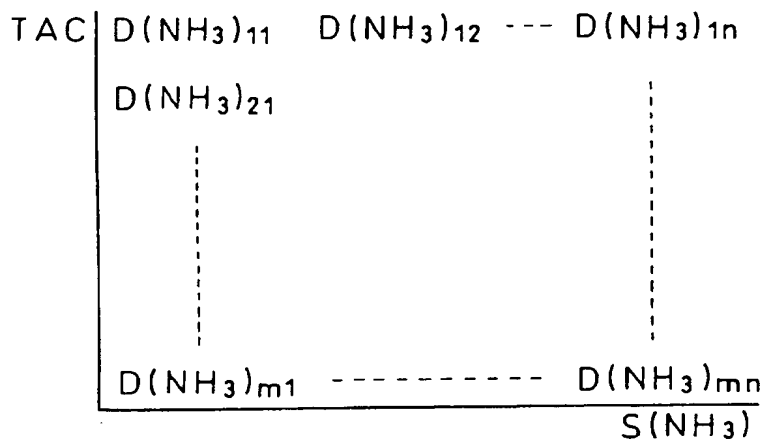


Fig.8B



WO 97/17532

PCT/JP96/03205

9/44

Fig.9A

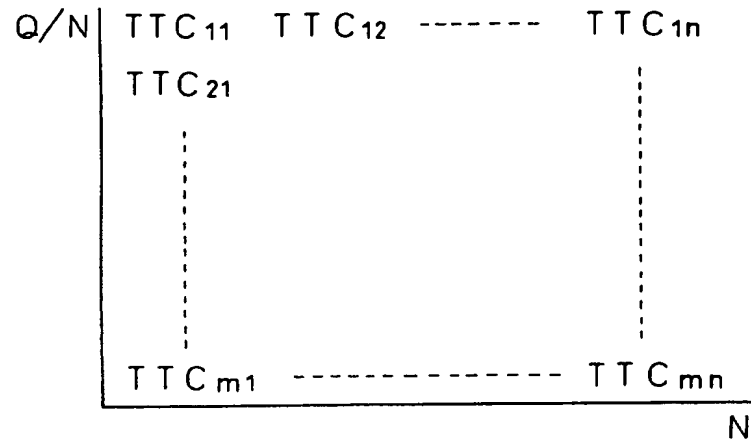
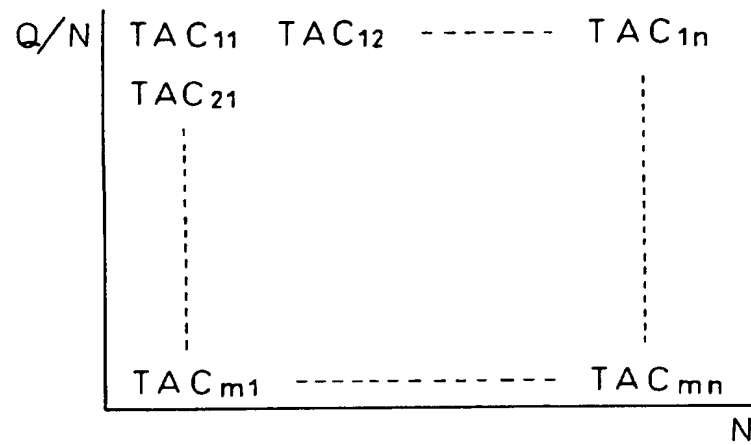


Fig.9B

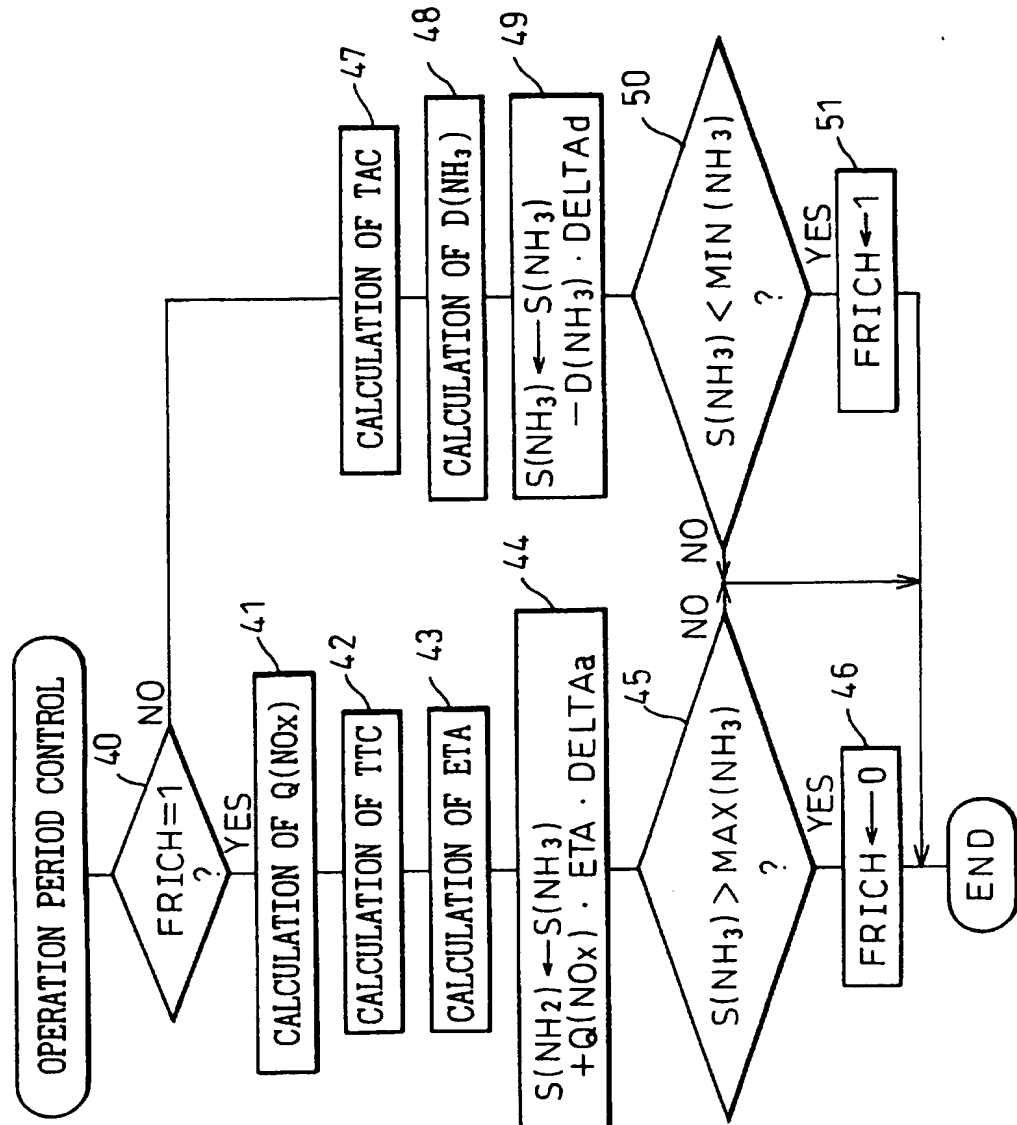


WO 97/17532

PCT/JP96/03205

10/44

Fig.10

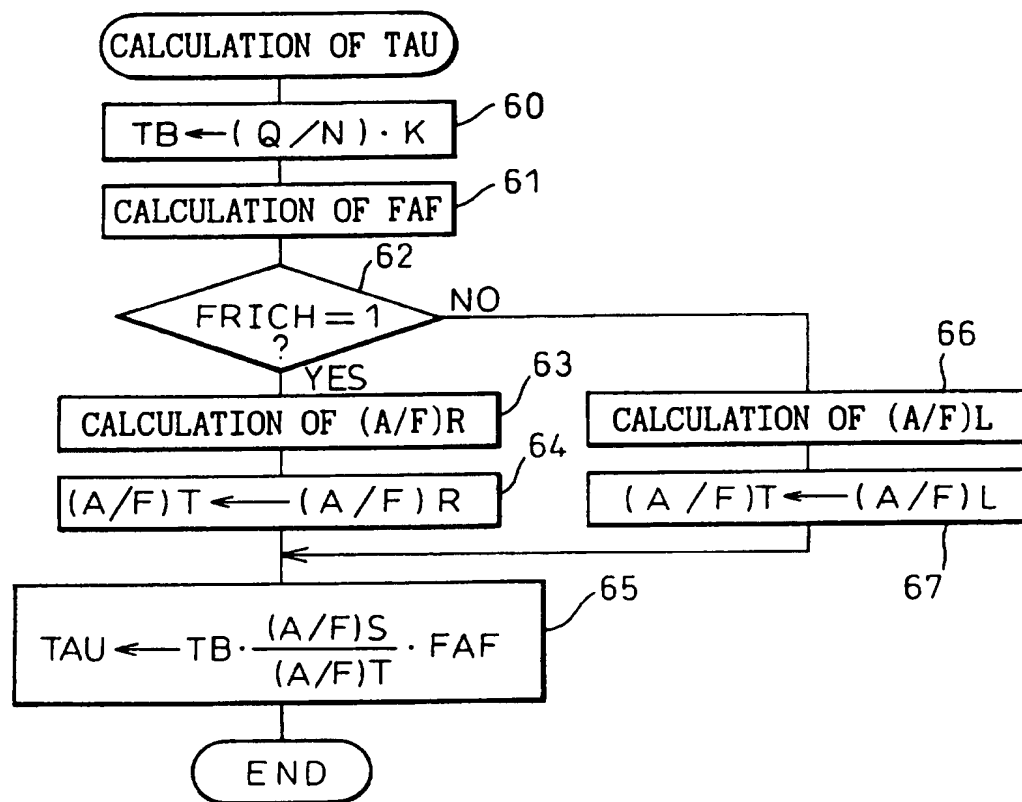


WO 97/17532

PCT/JP96/03205

11/44

Fig.11



WO 97/17532

PCT/JP96/03205

12/44

Fig. 12

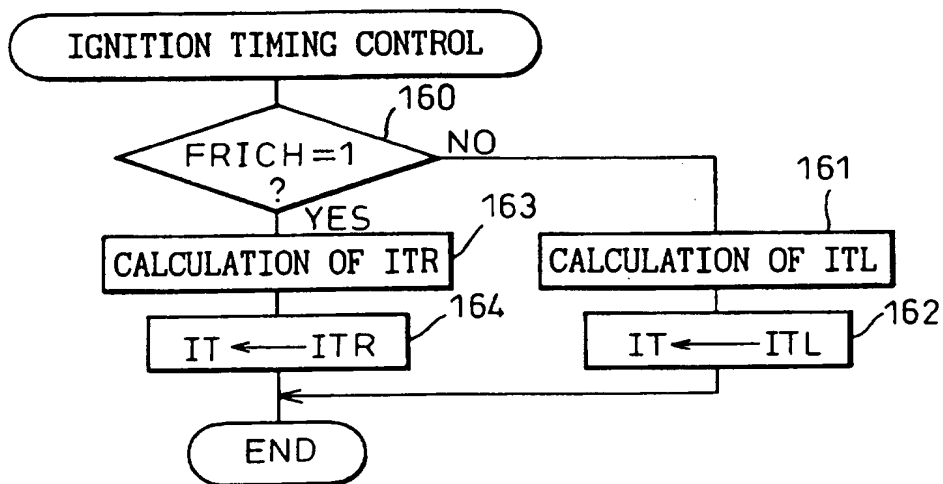
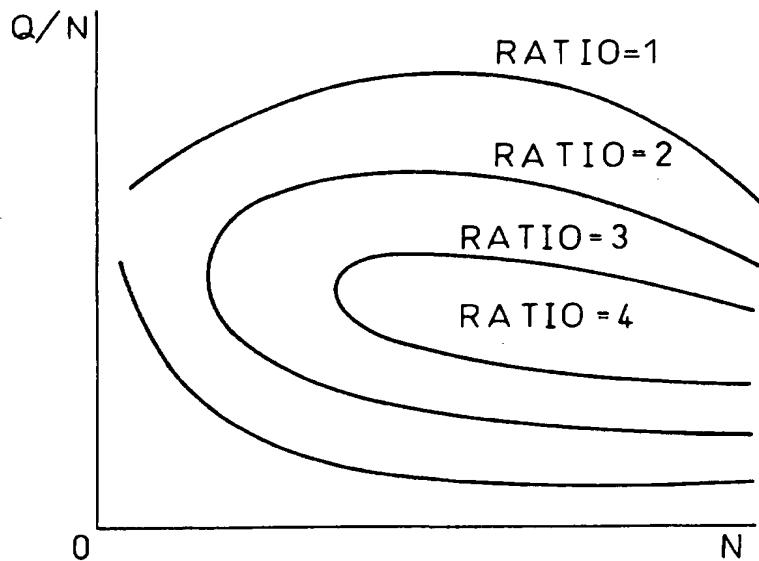


Fig. 13



WO 97/17532

PCT/JP96/03205

13/44

Fig.14

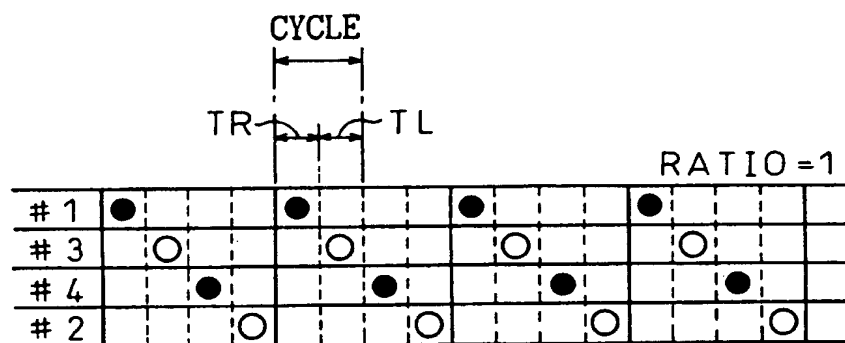
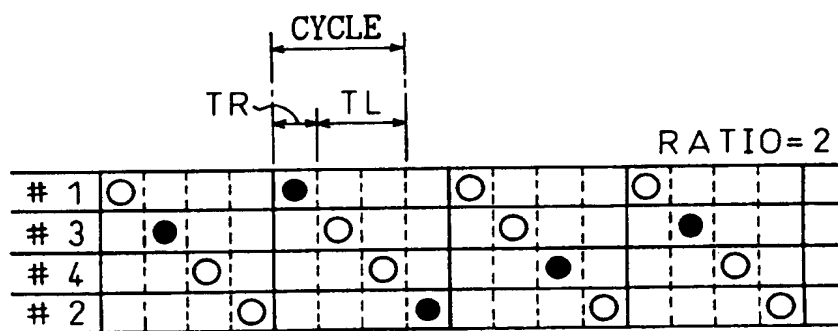


Fig.15



WO 97/17532

PCT/JP96/03205

$\frac{14}{44}$

Fig.16

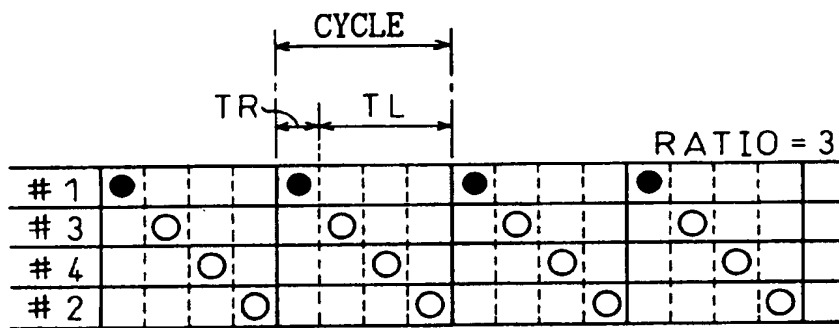
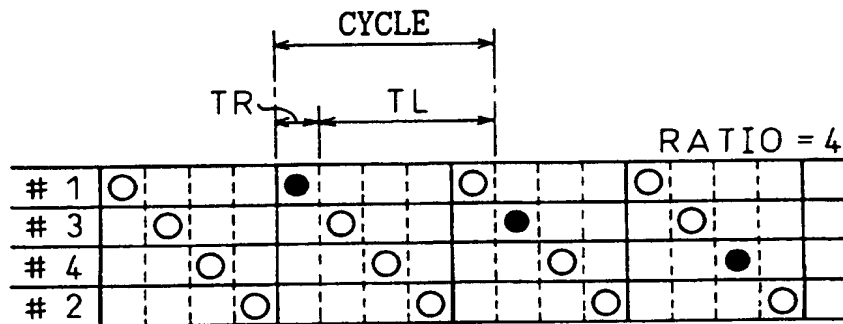


Fig.17



WO 97/17532

PCT/JP96/03205

15/
44

Fig.18

RATIO	1	2	3	4
DRATIO	00001	00011	00111	01111

Fig.19

RATIO = 2

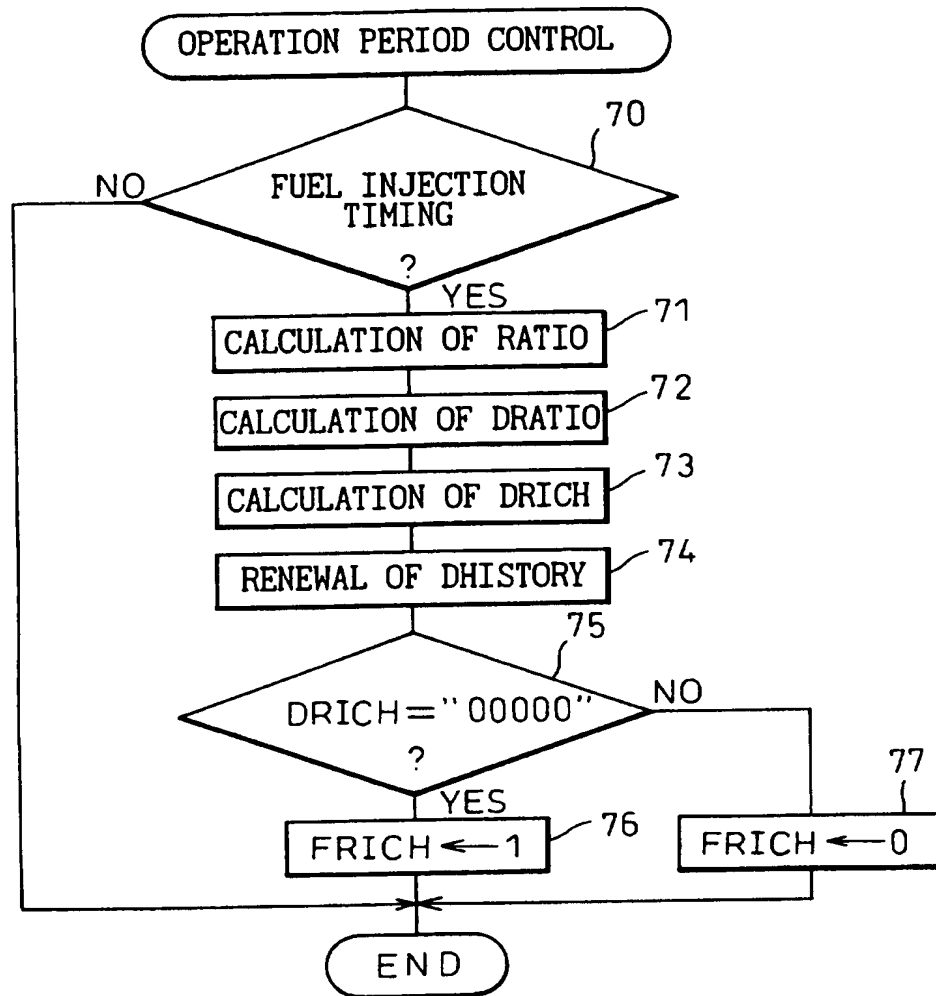
CYLINDER	# 2	# 1	# 3	# 4	# 2	# 1
DHISTORY	10010	00100	01001	10010	00100	01001
DRATIO	00011	00011	00011	00011	00011	00011
DRICH	00010	00000	00001	00010	00000	00001

WO 97/17532

PCT/JP96/03205

16/
44

Fig. 20



WO 97/17532

PCT/JP96/03205

17/
44

Fig.21

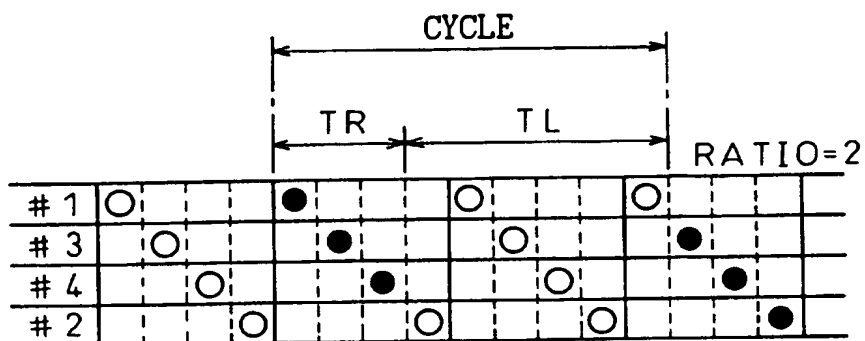
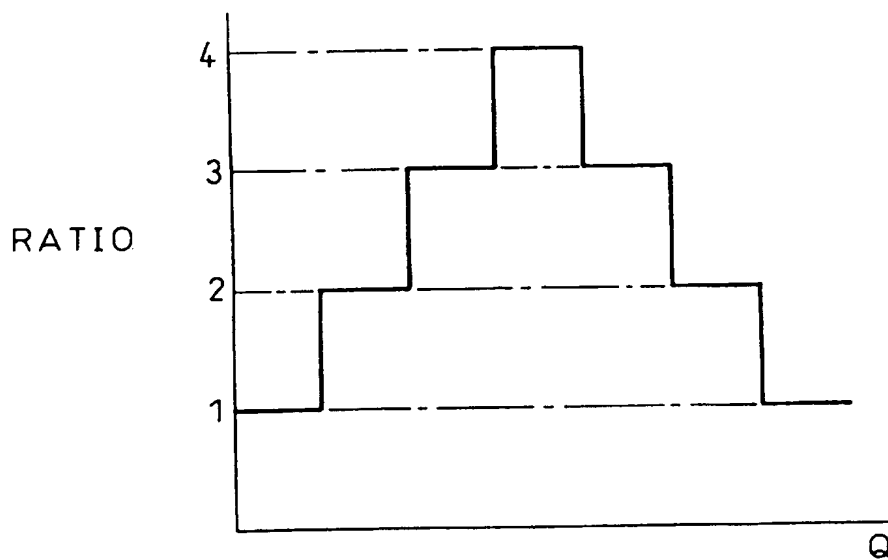


Fig.22



WO 97/17532

PCT/JP96/03205

$\frac{18}{44}$

Fig.23

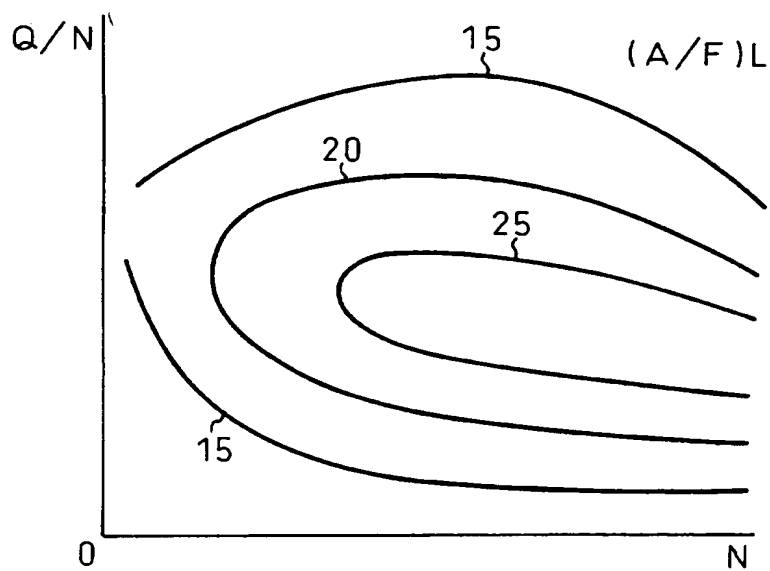
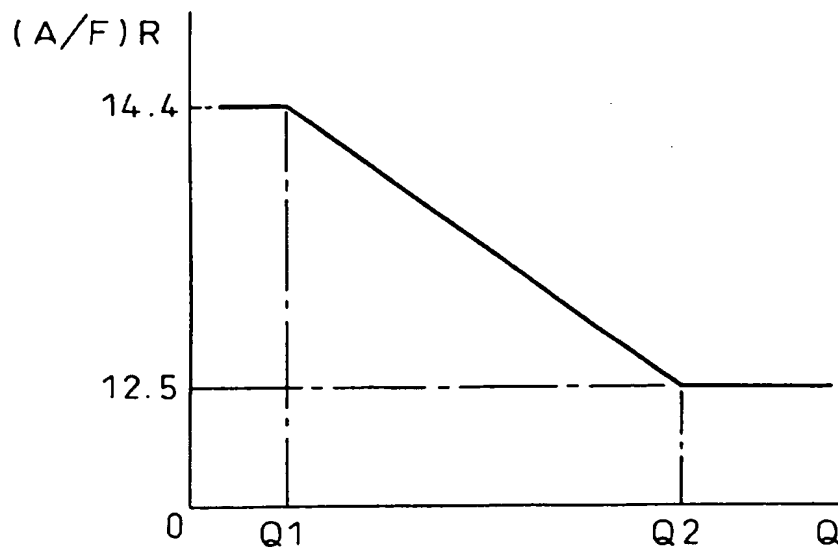


Fig.24



WO 97/17532

PCT/JP96/03205

19/
44

Fig .25A

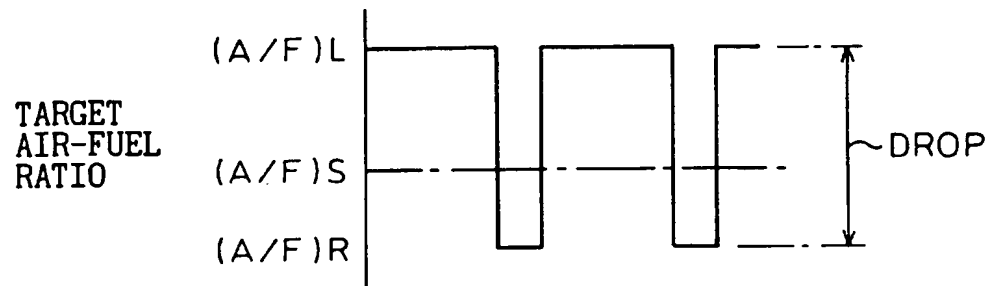
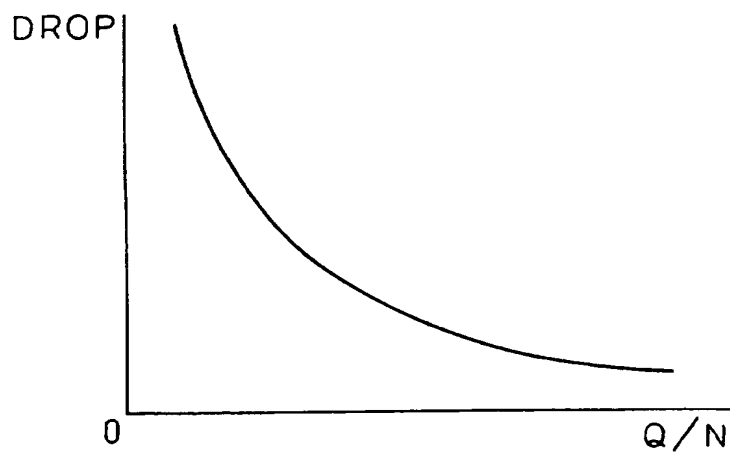


Fig .25B

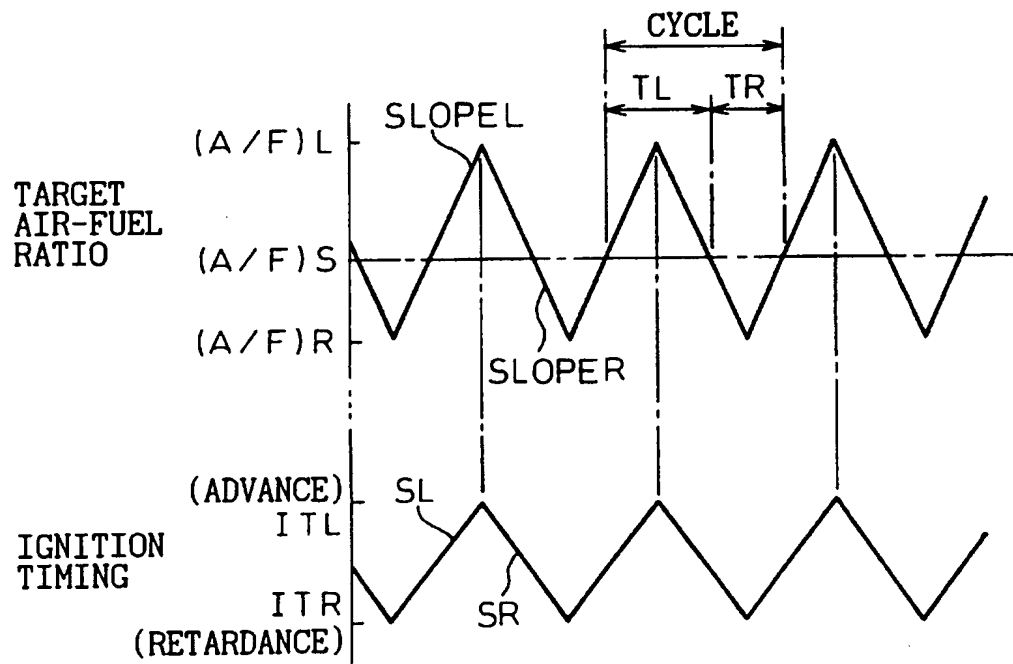


WO 97/17532

PCT/JP96/03205

20/44

Fig.26



WO 97/17532

PCT/JP96/03205

21/44

Fig.27

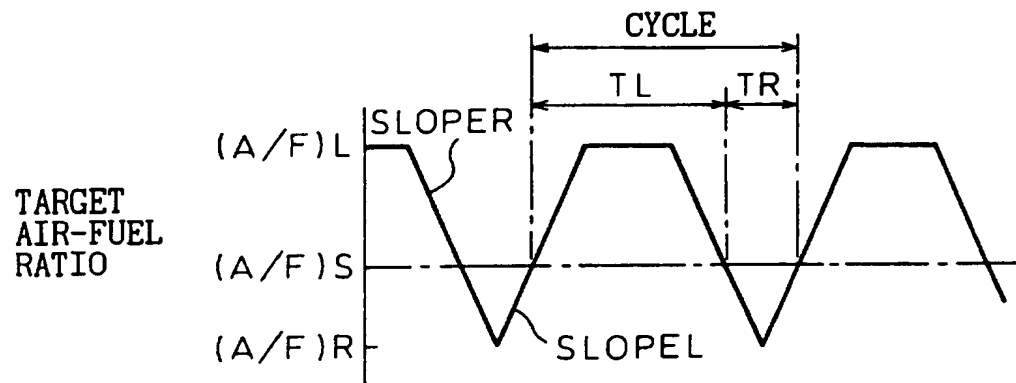
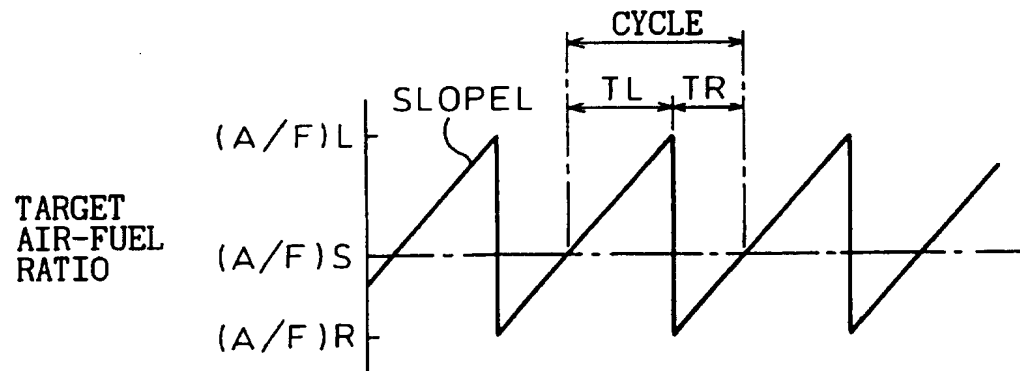


Fig.28



WO 97/17532

PCT/JP96/03205

22/44

Fig. 29

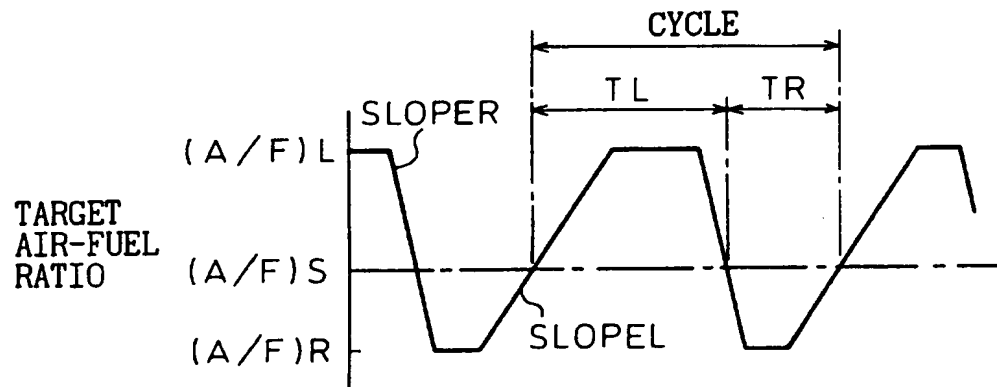
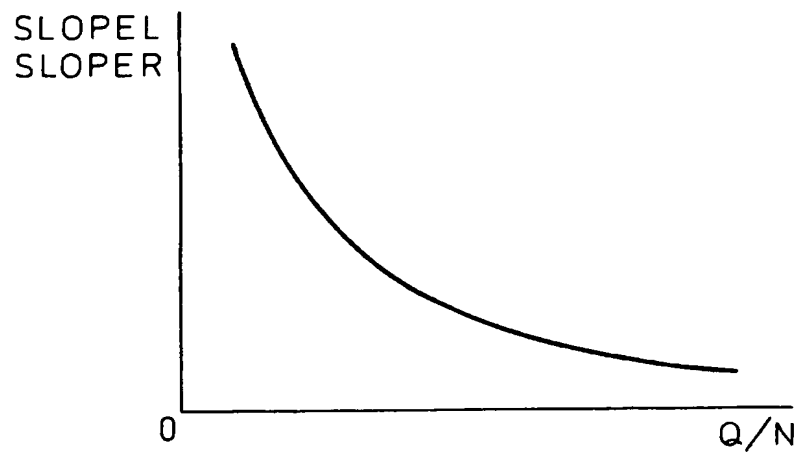
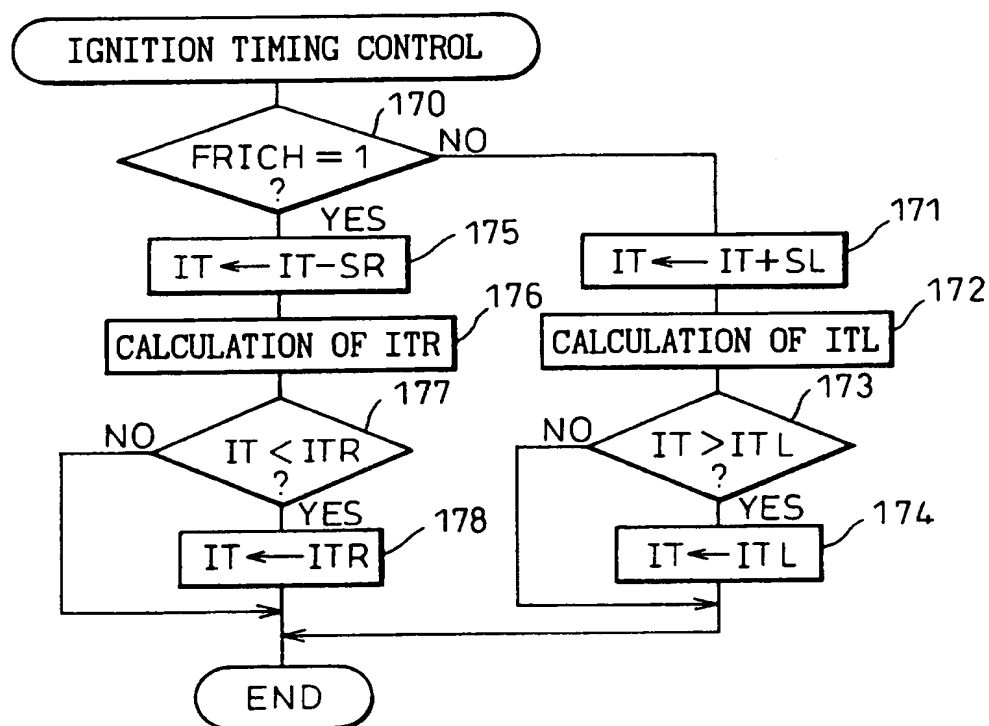


Fig. 30



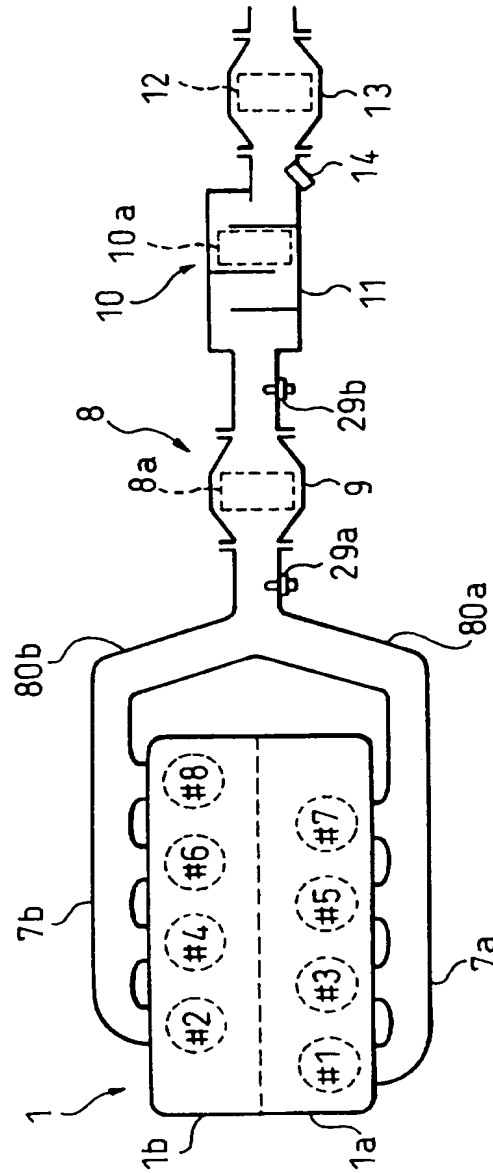
23/
44

Fig. 31



$$\frac{2L}{LL}$$

Fig. 32

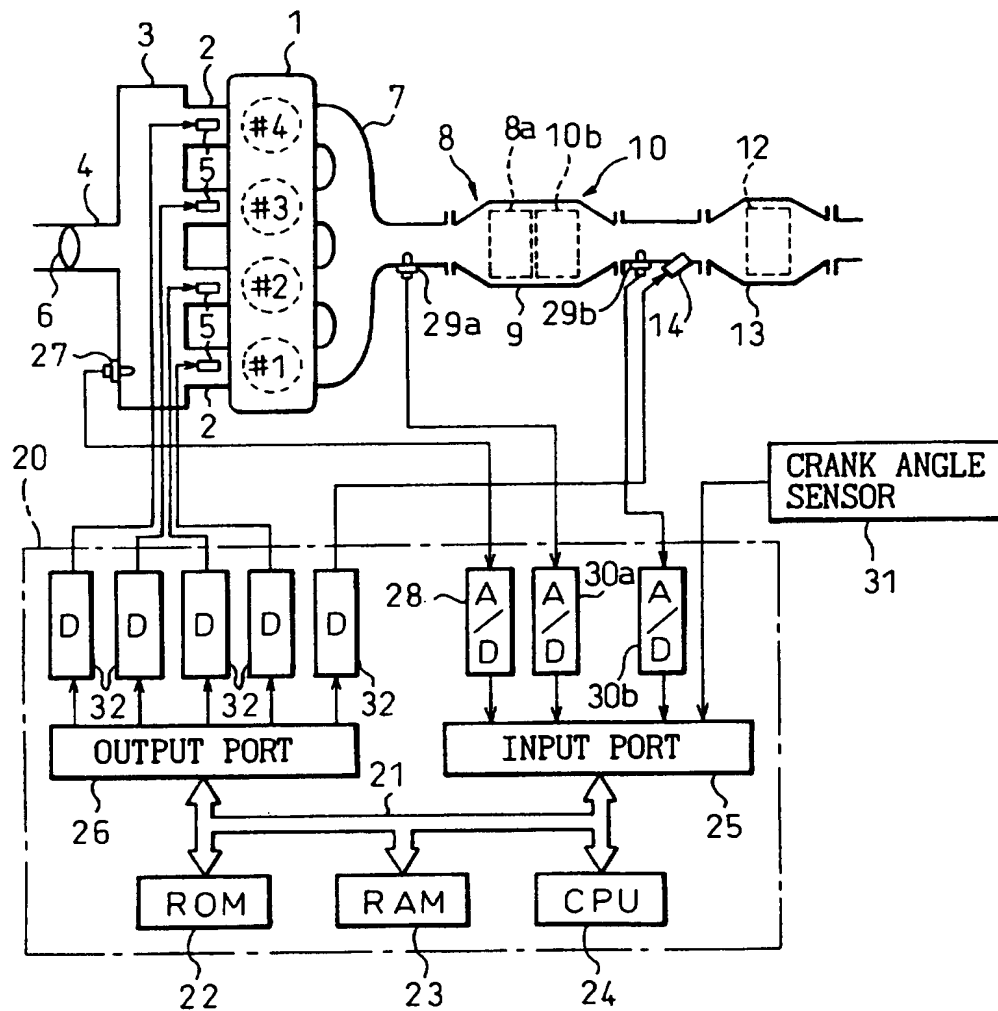


WO 97/17532

PCT/JP96/03205

25/44

Fig.33



WO 97/17532

PCT/JP96/03205

26/
44

Fig.34A

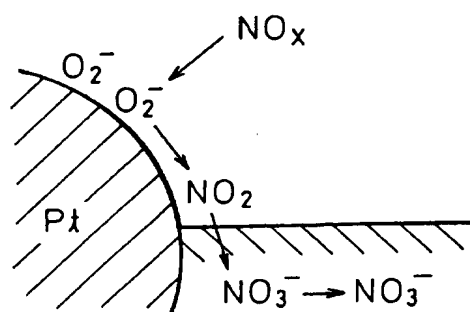
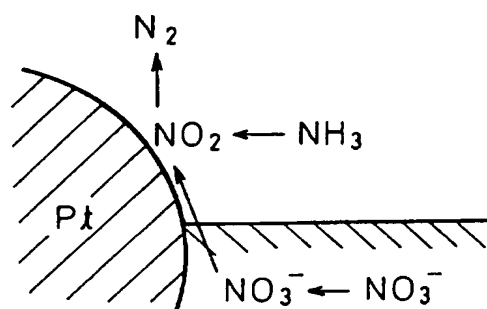


Fig.34B



27/44

Fig. 35A

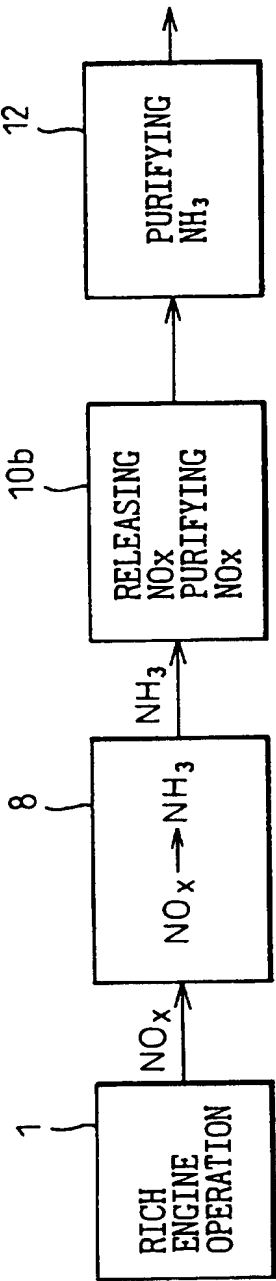
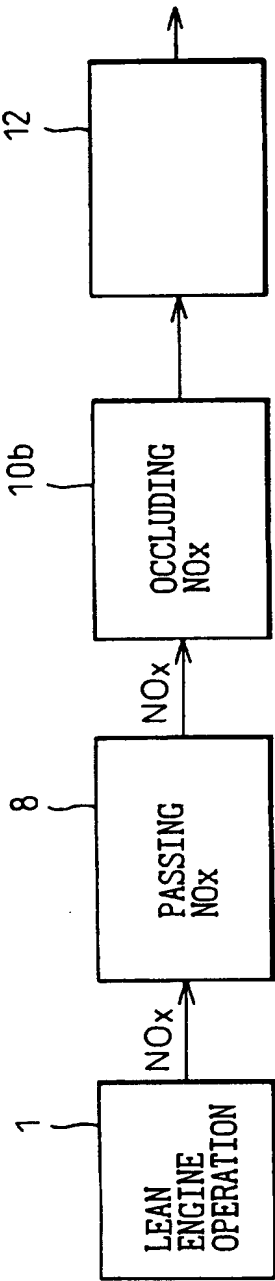


Fig. 35B



WO 97/17532

PCT/JP96/03205

28/
44

Fig.36A

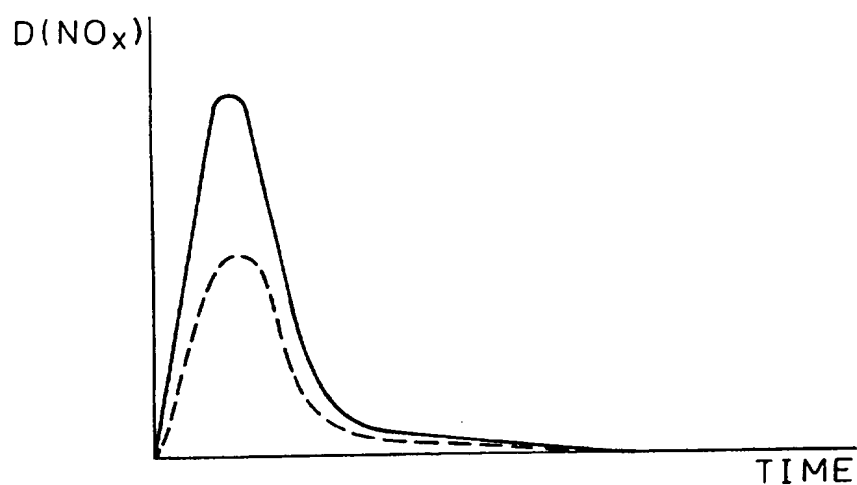
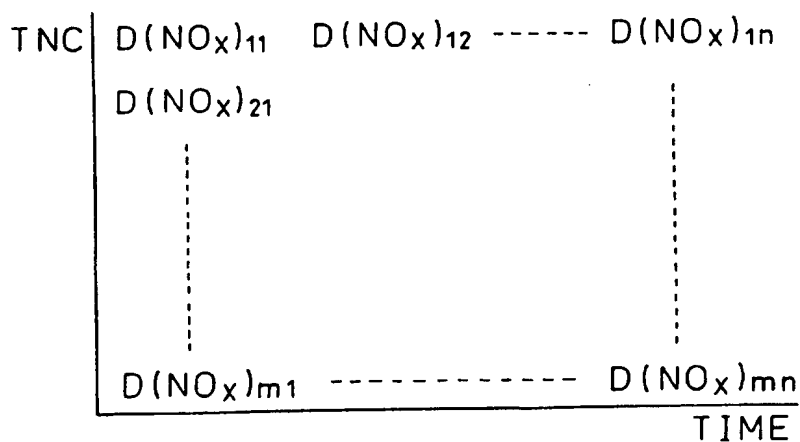


Fig.36B

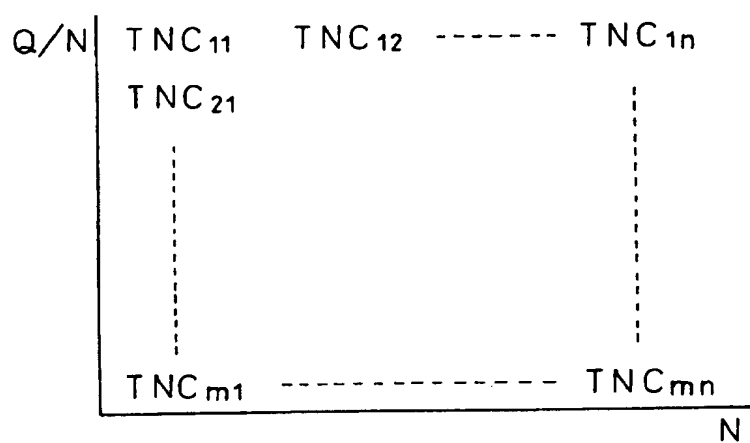


WO 97/17532

PCT/JP96/03205

29/
44

Fig.37

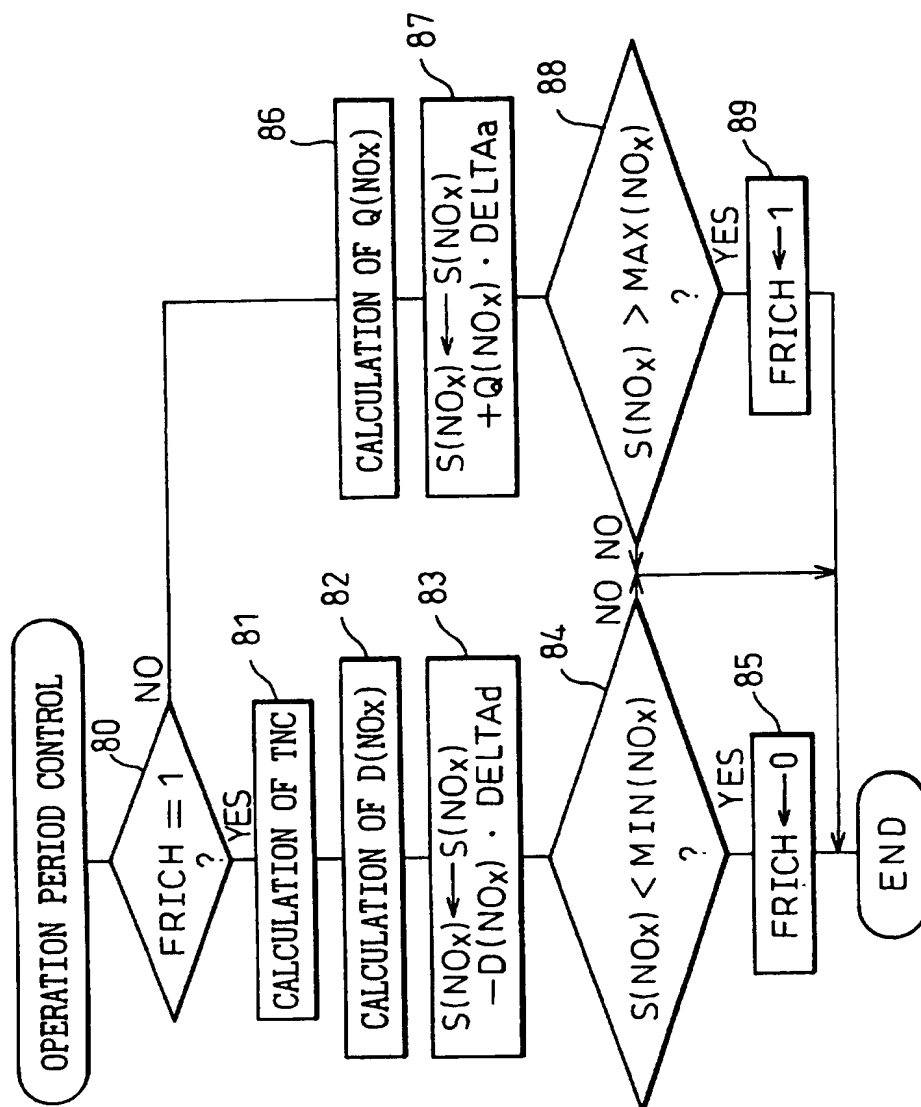


WO 97/17532

PCT/JP96/03205

30/44

Fig. 38A

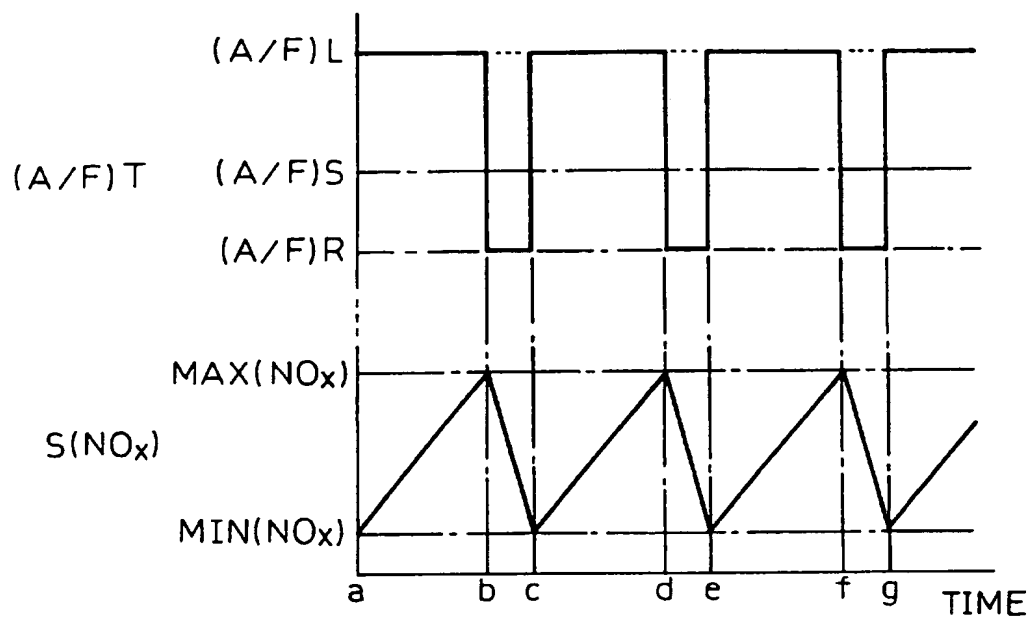


WO 97/17532

PCT/JP96/03205

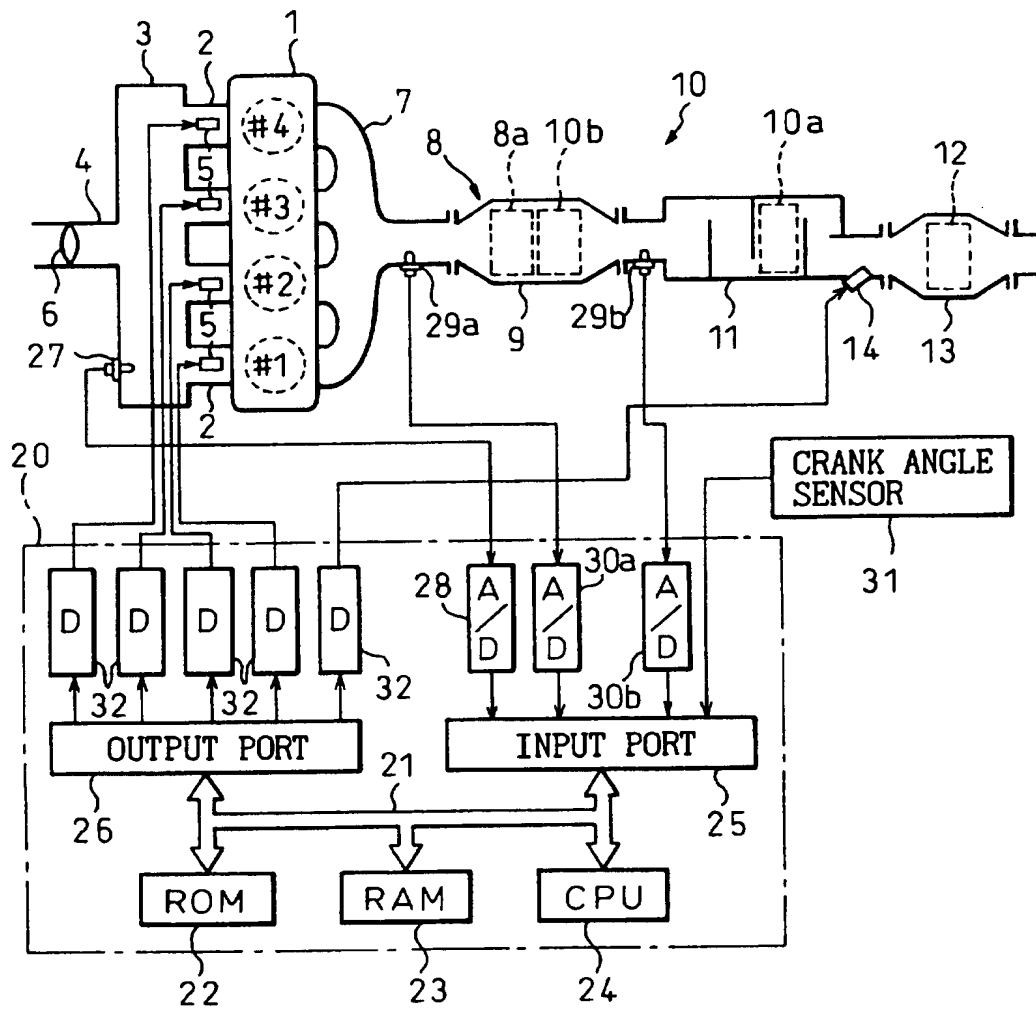
31/44

Fig. 38B



32/44

Fig. 39



33/44

Fig. 40A

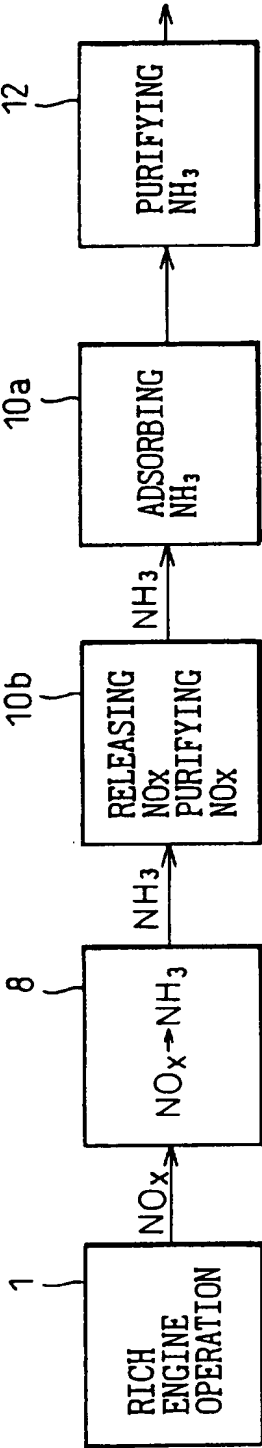
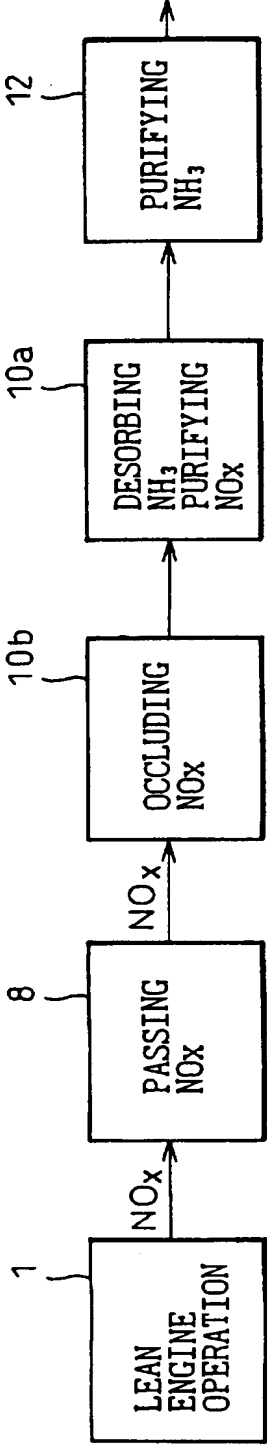


Fig. 40B



WO 97/17532

PCT/JP96/03205

34/44

Fig. 41A

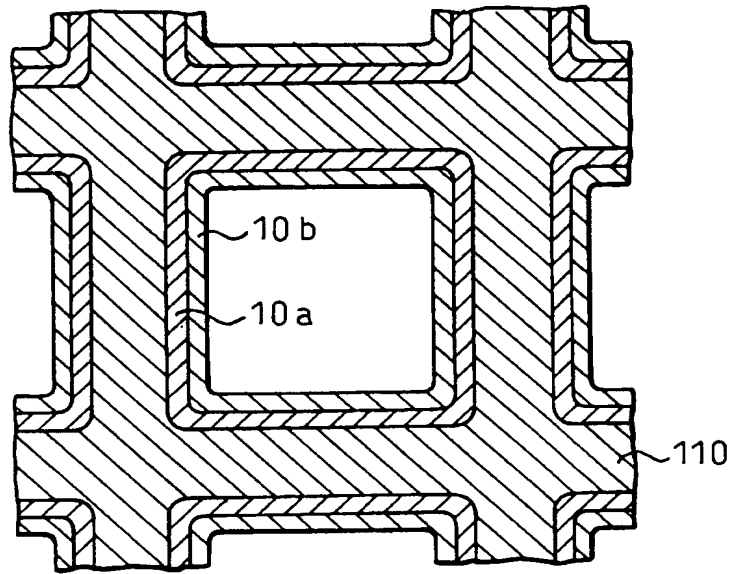
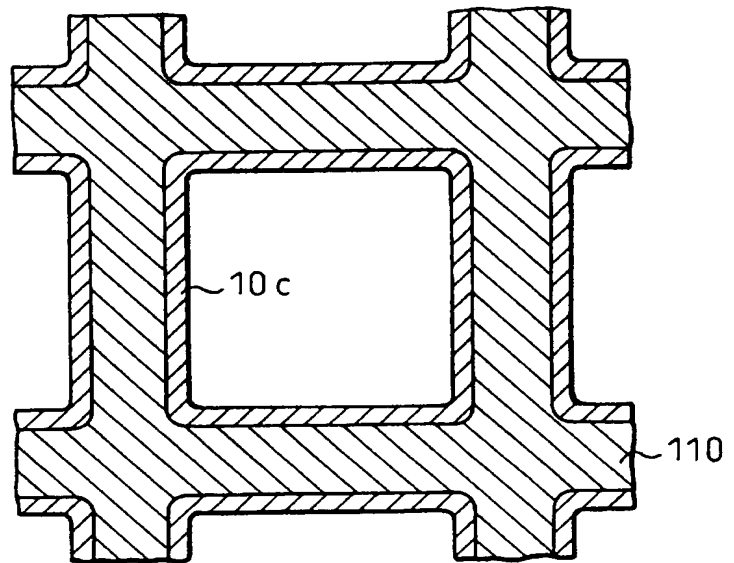
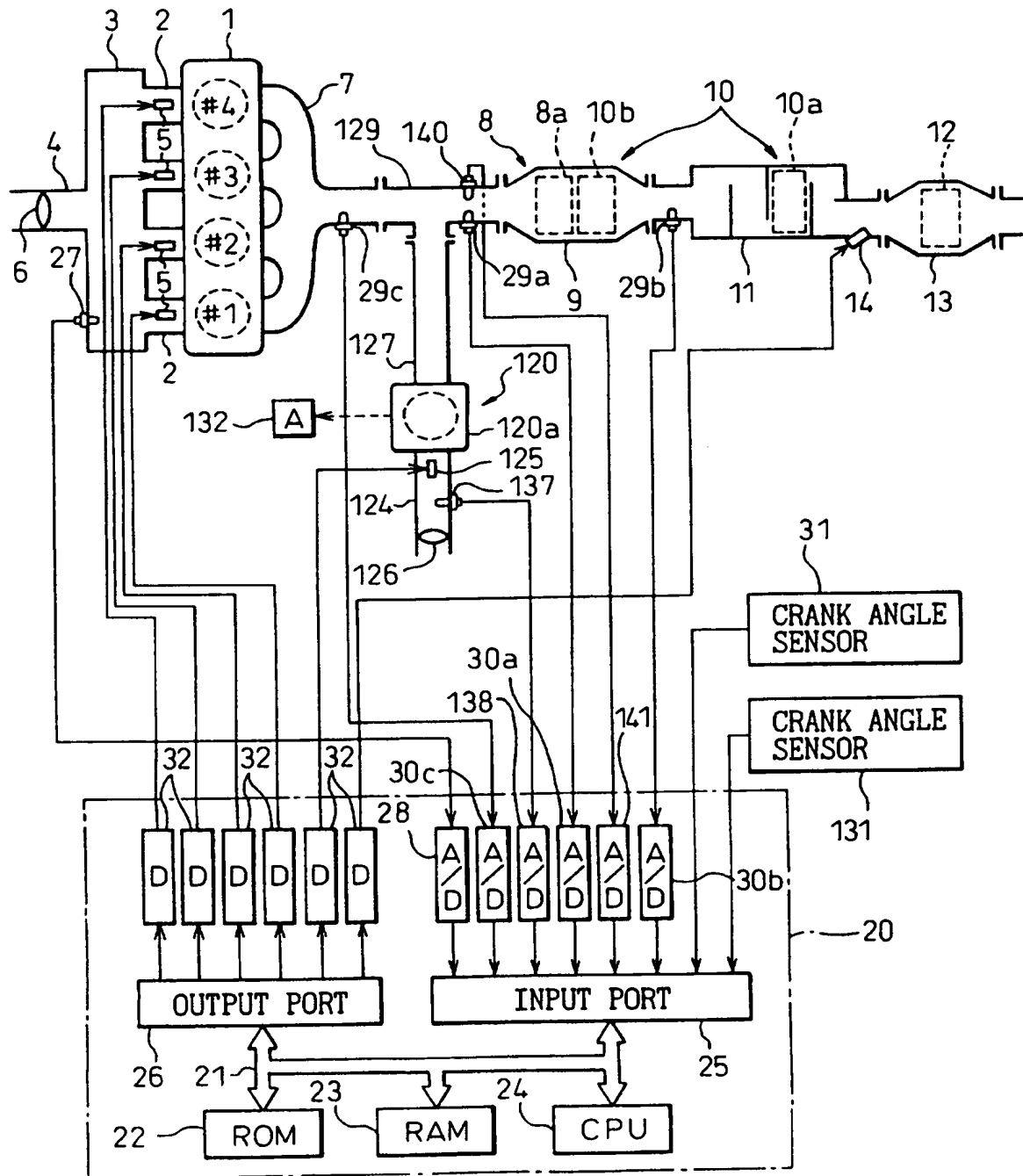


Fig. 41B



35/44

Fig. 42

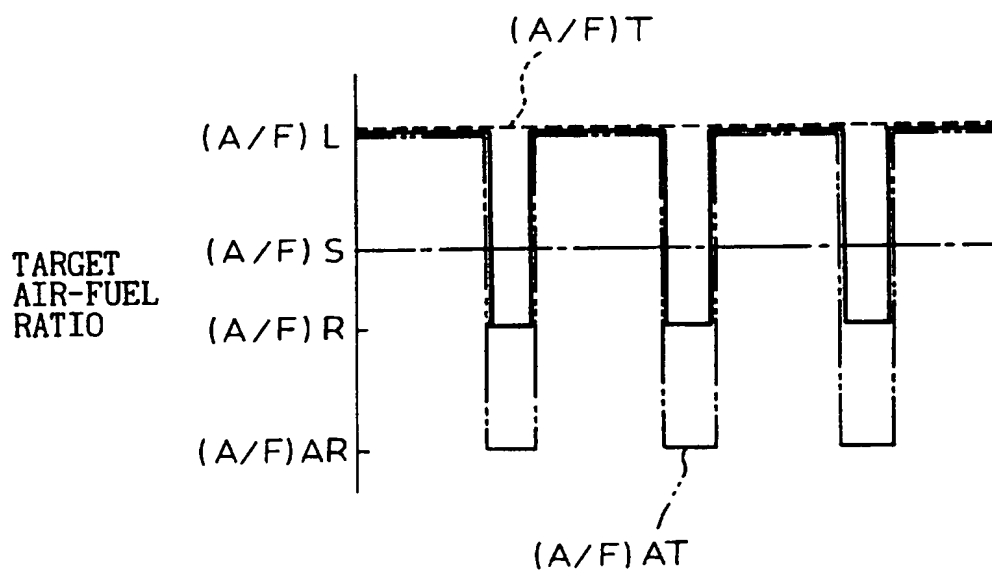


WO 97/17532

PCT/JP96/03205

36/
44

Fig. 43A

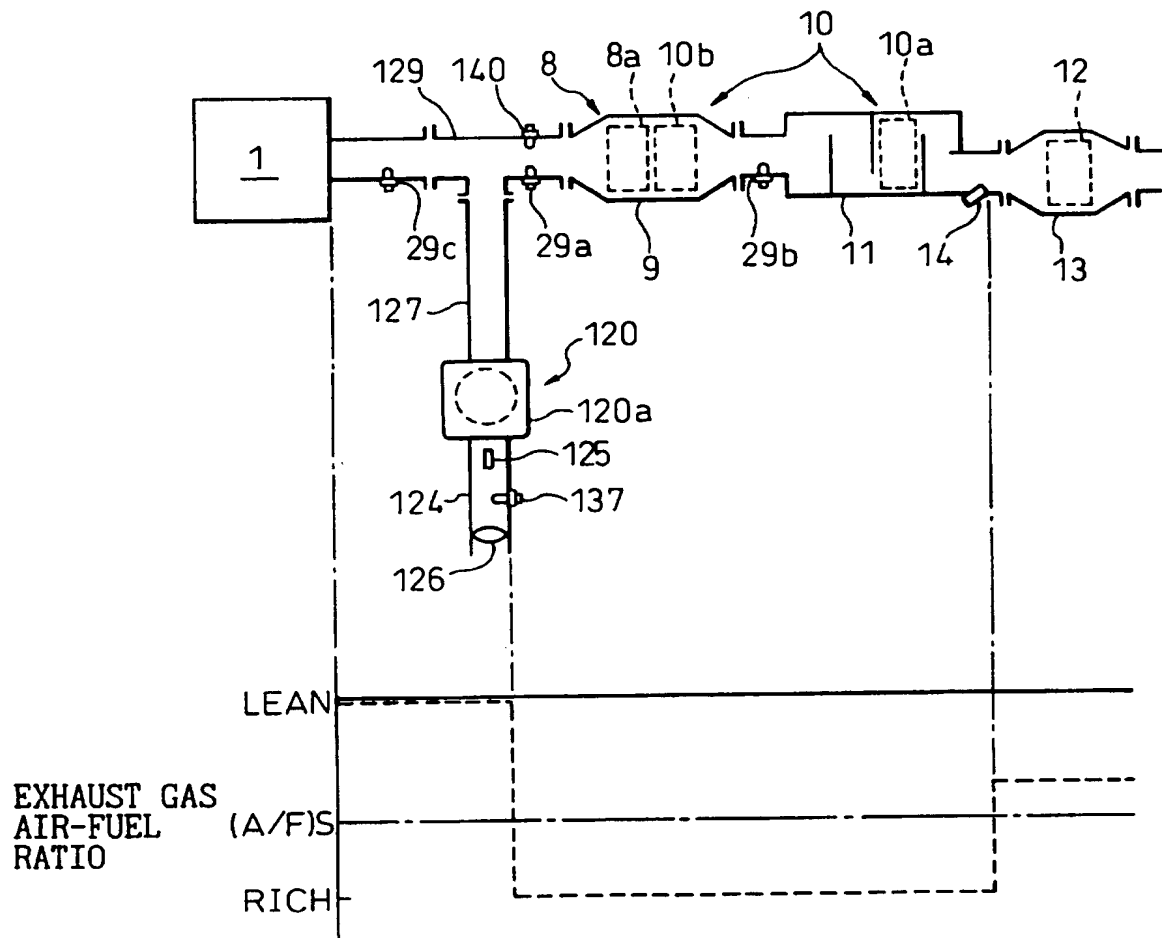


WO 97/17532

PCT/JP96/03205

37/44

Fig. 43B

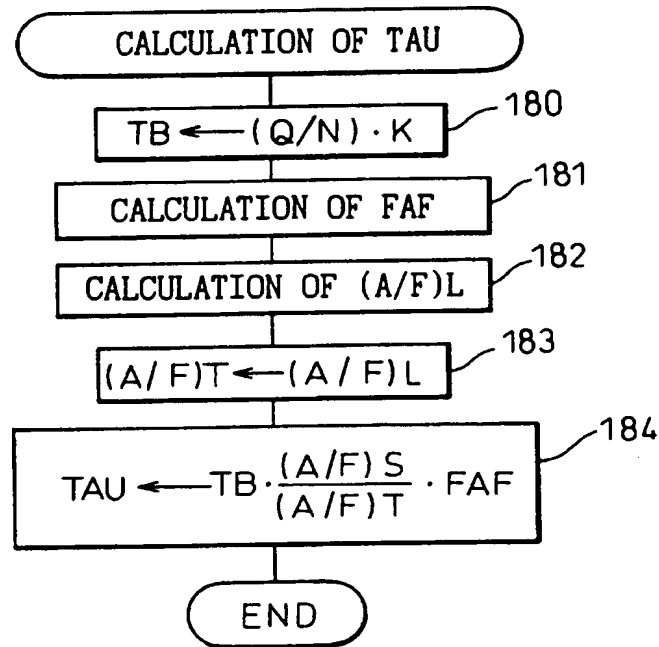


WO 97/17532

PCT/JP96/03205

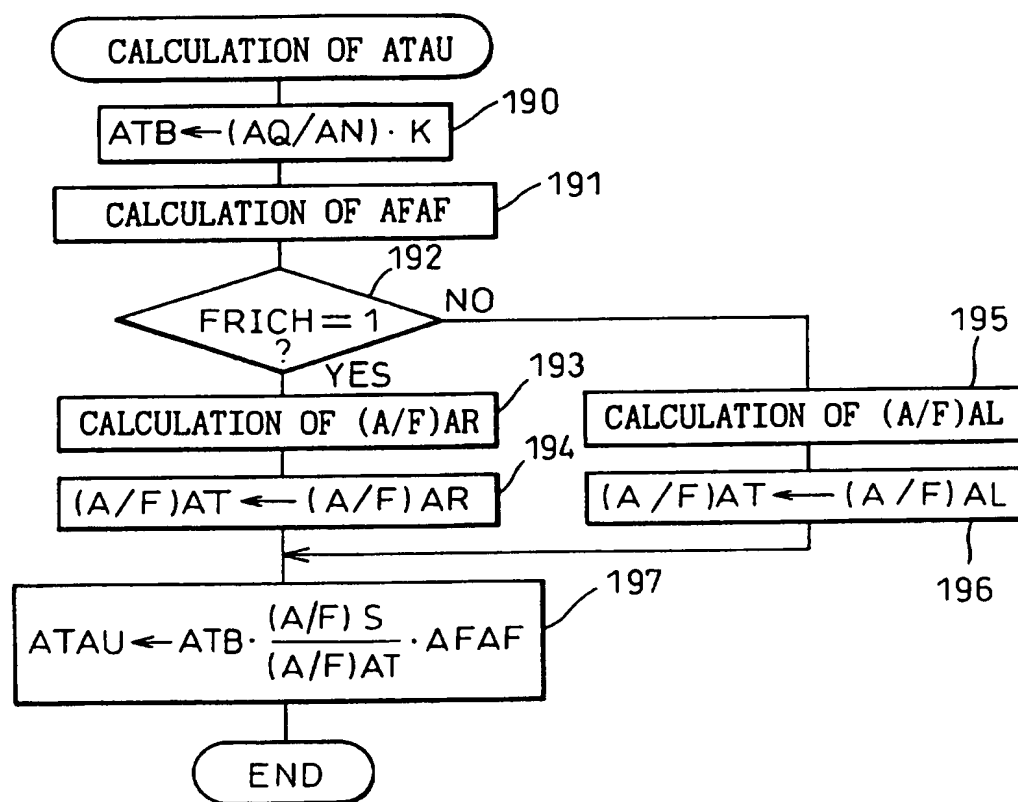
38/44

Fig. 44



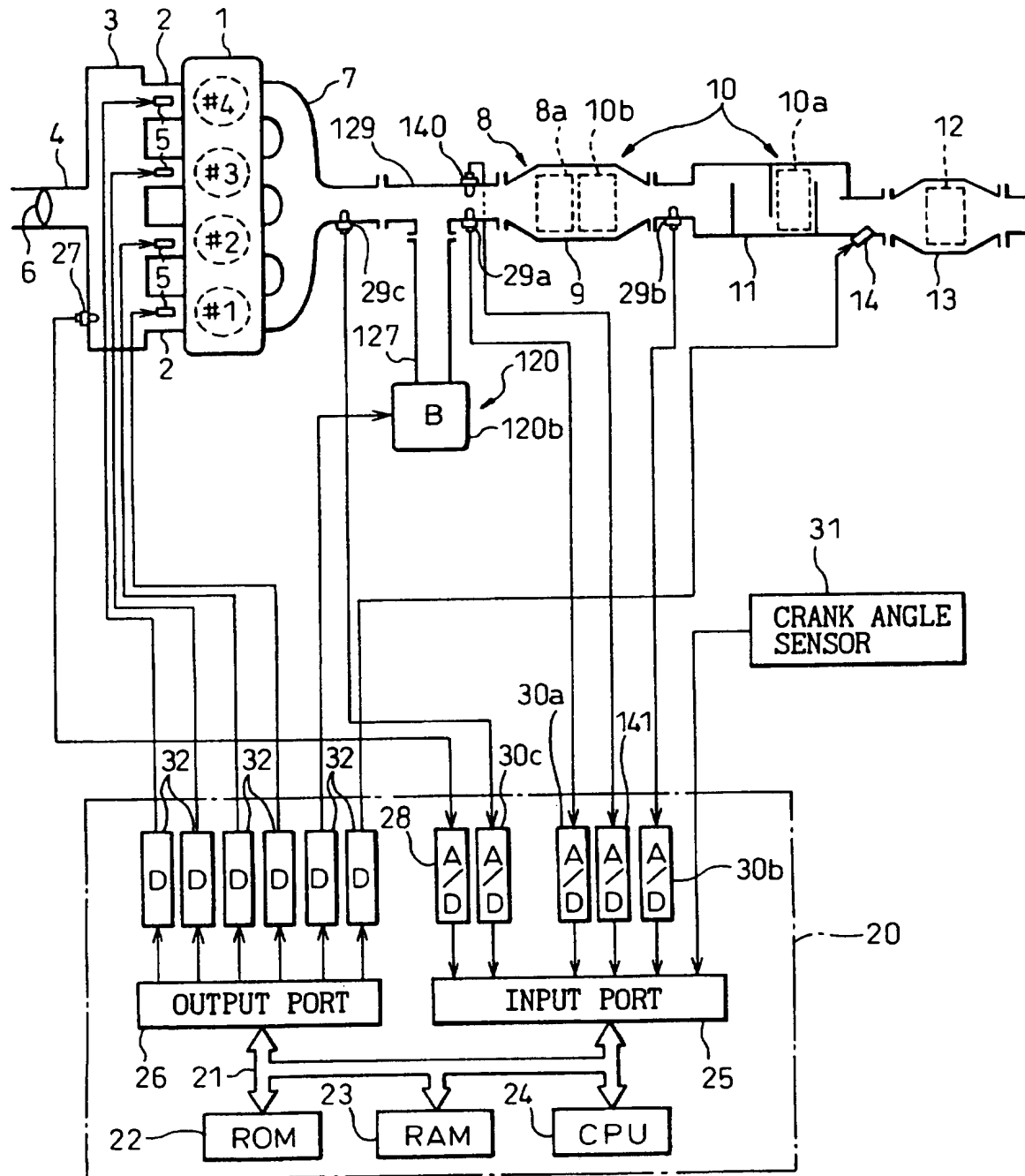
39/44

Fig. 45



40/44

Fig. 46

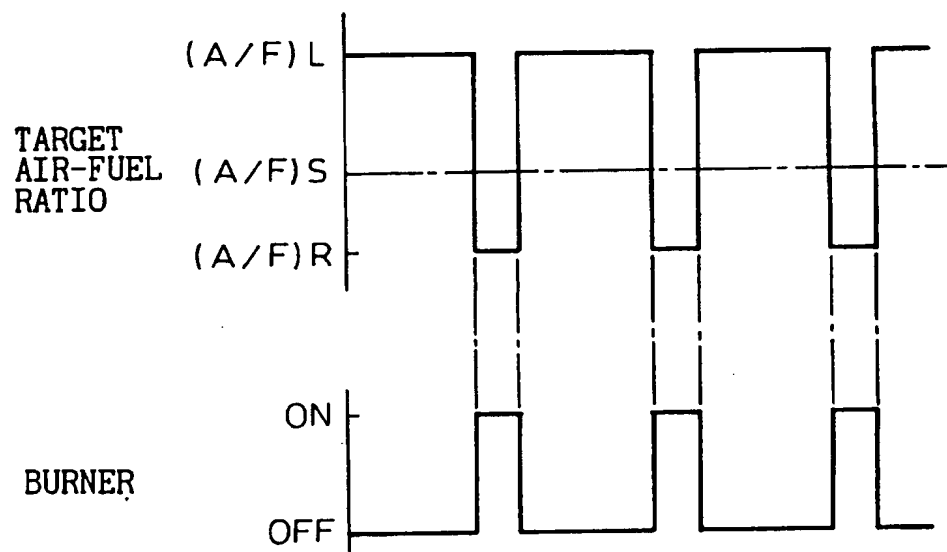


WO 97/17532

PCT/JP96/03205

41/
44

Fig. 47

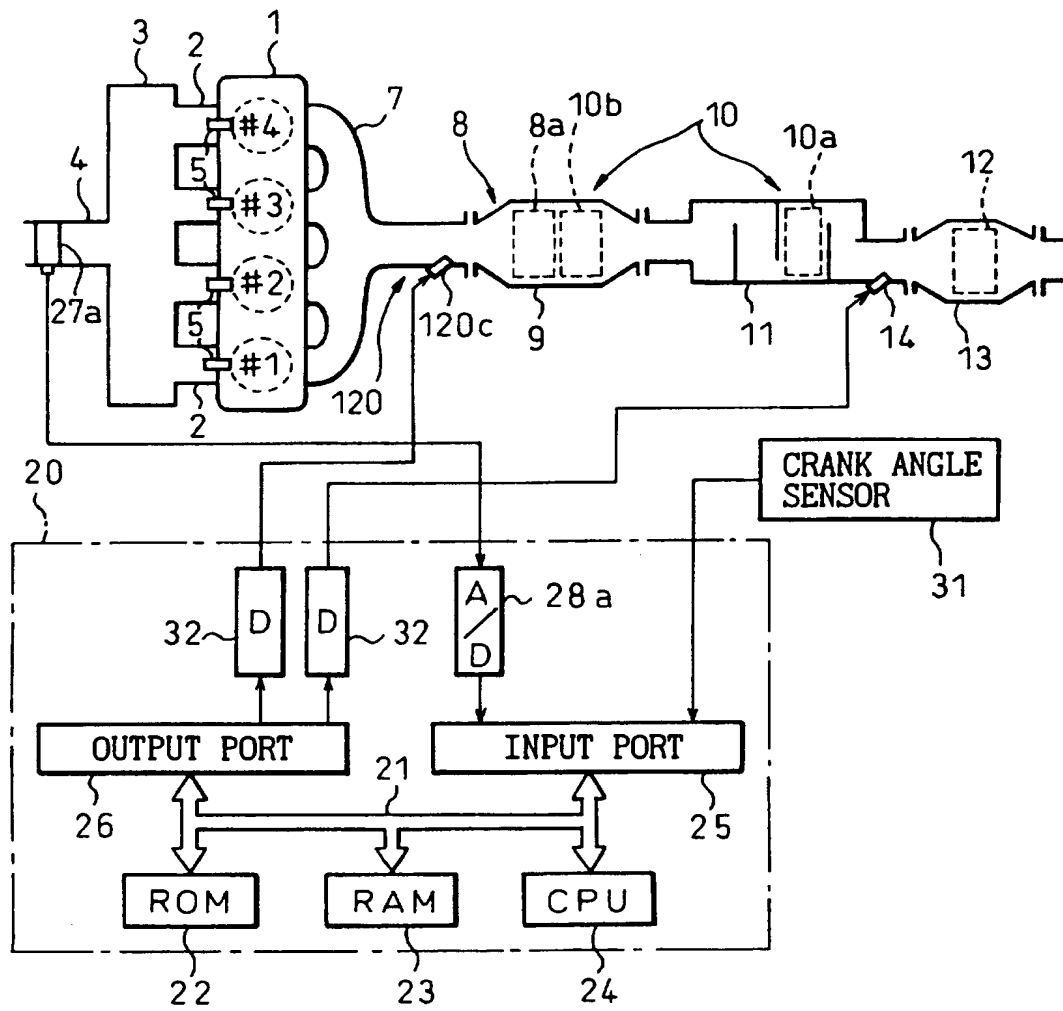


WO 97/17532

PCT/JP96/03205

42/44

Fig. 48

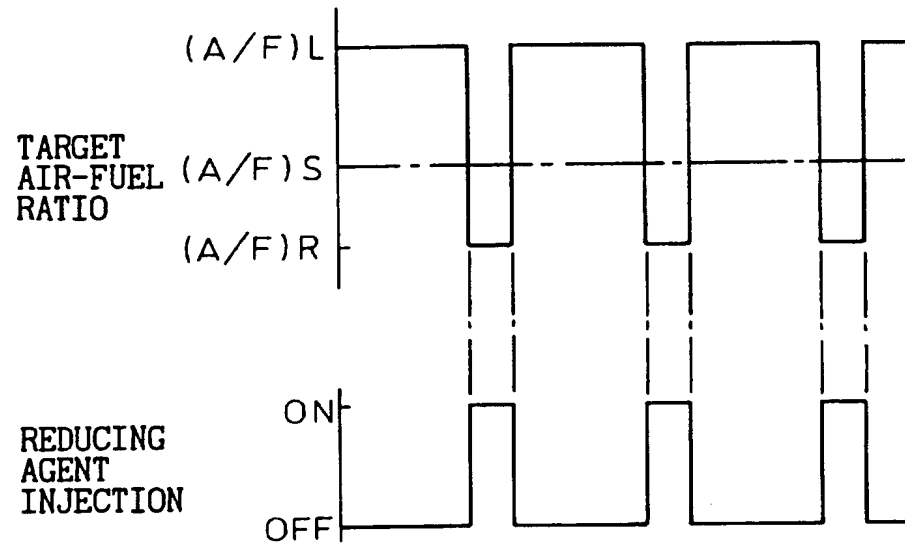


WO 97/17532

PCT/JP96/03205

43/
44

Fig. 49



WO 97/17532

PCT/JP96/03205

44 / 44

LIST OF REFERENCE NUMERALS

- 1 ... engine
- 5 ... fuel injector
- 7 ... exhaust manifold
- 8 ... NH₃ synthesizing catalyst
- 8a ... three way (TW) catalyst
- 10 ... exhaust gas purifying catalyst
- 10a ... NH₃ adsorbing and oxidizing (NH₃-AO) catalyst
- 10b ... NO_x occluding and reducing (NO_x-OR) catalyst

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 96/03205

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 F01N3/08 F01N9/00 B01D53/94 F01N3/28 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 F01N B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 240 (M-1409), 14 May 1993 & JP 04 365920 A (TOYOTA CENTRAL RES & DEV LAB INC; OTHERS: 01), 17 December 1992, cited in the application see abstract ---	1-6,10, 17,22, 26,31, 34, 47-52, 63,68, 72,77
A	EP 0 510 498 A (CORNING INC) 28 October 1992 see column 7, line 29 - column 14, line 48; figures --- -/-	1,11,12, 14, 42-47, 57,58, 60,88-91

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

A document member of the same patent family

Date of the actual completion of the international search

3 March 1997

Date of mailing of the international search report

10.03.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Sideris, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 96/03205

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 036 (M-1205), 29 January 1992 & JP 03 244915 A (MITSUBISHI HEAVY IND LTD), 31 October 1991, see abstract	1, 11, 12, 14-16, 47, 57, 58, 60-62
P, A	EP 0 701 858 A (TOYOTA MOTOR CO LTD) 20 March 1996	
A	US 3 825 654 A (KOBYLINSKI T ET AL) 23 July 1974	
A	GB 1 453 456 A (TOYODA CHUO KENKYUSHO KK) 20 October 1976	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 96/03205

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0510498 A	28-10-92	AT 148368 T AU 650120 B AU 1491592 A AU 8898891 A JP 5131118 A	15-02-97 09-06-94 29-10-92 29-10-92 28-05-93
EP 0701858 A	20-03-96	JP 8135437 A	28-05-96
US 3825654 A	23-07-74	NONE	
GB 1453456 A	20-10-76	JP 1033368 C JP 49071313 A JP 55018539 B	20-02-81 10-07-74 20-05-80